HELLMANN-FEYNMAN FORCES
AND DIPOLE MOMENTS USING
MULTIPLE-SCATTERING Xα WAVEFUNCTIONS
FOR DIATOMIC MOLECULES

By

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A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1975

ACKNOWLEDGEMENTS

The author would like to express his gratitude to Professor John W. D. Connolly who suggested the topic of this study and would like to thank him for his guidance, instruction and criticisms during this research.

The author would also like to acknowledge the other members of his advisory committee for their suggestions and criticisms. Also, thanks are due to all my other colleagues of the Quantum Theory Project at the University of Florida. The author particularly extends his appreciation to Dr. B. Danese for his many valuable discussions, continuous encouragement and especially for providing the author with his non-muffin-tin total energy program.

Finally, the author would like to thank his wife for her patience and encouragement.

This research was supported in part by the grant from the National Science Foundation which is also appreciated.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Abstract of Dissertation Presented to the Graduate Council
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

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December, 1975

Chairman: John W. D. Connolly
Major Department: Physics

The Hellmann-Feynman forces for H_2 and N_2, and the
dipole moments for LiH, BH and CH are calculated with the
Multiple-Scattering Xα wavefunctions. First, the muffin-tin
charge density approximation is used to compute these two
quantities. The results show that the internuclear forces
for homonuclear diatomic molecules are always repulsive, and
the dipole moments for LiH, BH and CH are far from the correct
values. Thus, it is necessary to use the non-muffin-tin charge
density in such molecular property calculations. The main
difficulty in such non-muffin-tin calculations is to evaluate
some three-dimensional integrals over the intersphere region.
To achieve this, we express the integrands in Prolate Spher-
oidal Coordinates and reduce the integrals into some one-di-
mensional integrals. The results show that both the force cal-
culations and the dipole moment calculations improve a lot
over the use of the muffin-tin charge density approximation.
For H_2, the Hellmann-Feynman force curve is obtained and com-
pared with the curve for the derivative of the total energy,

thus checking whether the Hellmann-Feynman Theorem is valid for the MSXα wavefunctions. For N_2, the force components contributed by each of the electronic states are calculated at the experimental equilibrium separation and are compared with the Hartree-Fock results. For LiH, BH and CH, the dipole moments thus obtained are respectively 7.29 D, -1.24 D and -1.958 D at the experimental equilibrium separations. Also, the derivative of the dipole moment for LiH at the equilibrium separation is obtained to be 1.27 D/a.u. We conclude that the non-muffin-tin correction is important in the force and dipole moment calculations. Any further improvement has to come from the correction to the MSXα wavefunctions.

CHAPTER I

INTRODUCTION

In the investigation of the electronic structure
and properties of atoms, molecules and solids, we often
encounter the problem of treating the exchange-correlation
effect properly. The Xα theory suggested by Slater provides
us a good way to handle such a problem (see Slater(1972a)).
Together with the muffin-tin approximation, the Xα theory
can be used to investigate the molecular system in a prac-
tical and accurate way. Such a method, called the Multiple-
Scattering Xα method or the MSXα method, was first suggested
by Slater(1965) and then was implemented by Johnson(1966).

Many of the results obtained with the MSXα method
show that it gives better results in the description of
the one-electron features than do the ab initio SCF-LCAO
methods, and is significantly much faster in calculation
(see Connolly and Johnson(1973)). However, in many cases,
we find that the total energy as a function of molecular
conformation is inaccurate. The energy curves of many diatom-
ic molecules, e.g., show that the systems are unbound. It
was pointed out by Connolly (see Connolly and Johnson(1973))

1

that such a discrepancy may be mainly due to the muffin-tin approximation, not the Xα approximation, in the calculation of the total energy. The current version for calculating the total energy assumes the muffin-tin approximation for the charge density. The result may be improved by taking the charge density, instead of its muffin-tin part, gererated from the converged wavefunctions in the calculation. This was verified by Danese on the calculations of carbon and neon molecules (see Danese(1973)).

If the discrepancy in the total energy calculation is indeed due to the use of the muffin-tin part of the charge density and not the Xα approximation, and the result does improve by using the complete form of the charge density, then it will mean that the converged MSXα wavefunctions are not too far from the true Xα wavefunctions and it may be useful to employ the MSXα wavefunctions in other molecular property calculations. In this dissertation, we shall investigate the quality of these MSXα wavefunctions directly in the dipole moment and force calculations of some diatomic molecules.

It was proved by Slater (see Slater(1972b)) that the Hellmann-Feynman Theorem is satisfied by the exact Xα wavefunctions. That is, the quantum mechanical force acting on a nuclear coordinate is equal to the electrostatic force exerted by the other nuclei and the electronic charge cloud which is formed by the exact Xα wavefunctions. Thus, it is

useful to check the quality of the MSXα wavefunctions by
testing if the theorem is also valid for these approximated
Xα wavefunctions. Also, as it is well known that the dipole
moment is more sensitive to the wavefunction than is the
energy, it is useful to check the quality of the MSXα wave-
functions by doing some dipole moment calculations.

The difficulty in all these calculations is that
we have to evaluate some three-dimensional multi-center
integrals over an awkward region. In this dissertation, we
solve this difficulty by a computational technique which
reduces the integrals into one-dimensional integrals whose
integrands involve sine and cosine integrals. The main
point in this method is to employ the Prolate Spheroidal
Coordinates. It is hopeful that this method can be used in
some other molecular property calculations. We shall dis-
cuss it in detail in Chapter IV and Chapter V.

In Chapter II, we shall give a brief discussion of
the exact Xα method and the approximate MSXα method. In
Chapter III, we shall discuss the effect of assuming the
muffin-tin charge density in the calculation of total energy,
force and dipole moment, thus showing the necessity of using
the non-muffin charge density in the calculations. Chapter
IV will be devoted on the force calculations and Chapter V
will be devoted on the dipole moment calculations. Finally,
we shall conclude in Chapter VI.

CHAPTER II

EXACT Xα METHOD AND MUFFIN-TIN APPROXIMATE Xα METHOD

2.1 Introduction

The discussions in this chapter shall mainly concern
the basic Xα theory and also its muffin-tin approximate form
in the application to molecular systems. First, we shall
briefly discuss the basic Xα theory and its exact one-
electron Schrödinger equations, in which no specific restrict-
ion is placed on the form of the charge density and the
potential. Secondly, we shall discuss the MSXα method, in
which the charge density and the potential are muffin-tin
averaged. The approximate Xα one-electron Schrödinger equa-
tions and their solutions are discussed. The quality of
the solutions of the approximate Xα one-electron equations
is one of our main concerns in this dissertation.

2.2 Exact Xα One-Electron Schrödinger Equations

The Xα method was suggested by Slater and has been
discussed in detail by many others (see Slater(1972a),
Slater and Johnson(1972)).

The Xα one-electron Schrödinger equations for the

4

spin-orbitals $u_i(\vec{r})$ can be derived by the variational principle from an expression of spin up and spin down charge density:

$$\rho_\uparrow(\vec{r}) = \sum_{i\,\uparrow} n_i u_i^*(\vec{r}) u_i(\vec{r})$$

$$\rho_\downarrow(\vec{r}) = \sum_{i\,\downarrow} n_i u_i^*(\vec{r}) u_i(\vec{r})$$

where n_i are the occupation numbers and the summation is over the spin up and spin down orbitals respectively. Also we define the total charge density as

$$\rho(\vec{r}) = \rho_\uparrow(\vec{r}) + \rho_\downarrow(\vec{r})$$

Then the Xα total energy is

$$\langle E_{x\alpha} \rangle = \sum_i n_i \int u_i^*(\vec{r}_1)(-\nabla_1^2) u_i(\vec{r}_1) d\vec{r}_1$$

$$+ \int \sum_{p=1}^{N} \frac{-2Z_p}{|\vec{r}_1 - \vec{R}_p|} \rho(\vec{r}_1) d\vec{r}_1 + \frac{1}{2} \iint \frac{2\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2$$

$$+ \frac{1}{2} \int \rho_\uparrow(\vec{r}_1) U_{x\alpha}^\uparrow(\vec{r}_1) d\vec{r}_1 + \frac{1}{2} \int \rho_\downarrow(\vec{r}_1) U_{x\alpha}^\downarrow(\vec{r}_1) d\vec{r}_1$$

$$+ \frac{1}{2} \sum_{\substack{p,q \\ p \neq q}} \frac{2Z_p Z_q}{R_{pq}} \qquad (2.1)$$

Here the nuclear coordinates are $\vec{R}_p$ and their atomic numbers are Z_p. Rydbergs are used as units of energy, atomic units as units of distance. The first term is the kinetic energy. The second term is the nuclear-electron coulomb energy. The third term is the electron-electron coulomb interaction term. The fourth and the fifth are the "exchange-correlation" energy terms of either spin. The last one is

the nuclear-nuclear interaction term.

The above expression is exact except for the exchange-correlation term. Here we define it as:

$$U_{x\alpha}^{\uparrow}(\vec{r}) = -9\alpha((3/4\pi)\rho_{\uparrow}(\vec{r}))^{1/3} \qquad (2.2)$$

and similarly for $U_{x\alpha}^{\downarrow}(\vec{r})$.

The Xα total energy is a function of the occupation numbers n_i and a functional of the spin-orbitals u_i. It can be shown that if we vary the u_i to minimize the total energy with fixed occupation numbers n_i, we can get the Xα one-electron Schrödinger equations as:

$$\{-\nabla_1^2 + V_c(\rho,\vec{r}_1) + V_{x\alpha}(\rho,\vec{r}_1)\}\, u_i(\vec{r}_1) = \varepsilon_i\, u_i(\vec{r}_1) \qquad (2.3)$$

where

$$V_c(\rho,\vec{r}_1) = \sum_{p=1}^{N} \frac{-2Z_p}{|\vec{r}_1-\vec{R}_p|} + 2\int \frac{\rho(\vec{r}_2)}{r_{12}}\, d\vec{r} \qquad (2.4)$$

is the electrostatic potential at position $\vec{r}_1$, and

$$V_{x\alpha}(\rho,\vec{r}_1) = \left[\begin{array}{ll} -6\alpha((3/4\pi)\rho_{\uparrow}(\vec{r}_1))^{1/3} & \text{for spin up } u_i \\ \\ -6\alpha((3/4\pi)\rho_{\downarrow}(\vec{r}_1))^{1/3} & \text{for spin down } u_i \end{array} \right.$$

$$(2.5)$$

is the exchange correlation potential at $\vec{r}_1$.

Since the potential in the Xα one-electron equations is a functional of the spin-orbitals u_i, the Xα method is a self-consistent method. We start by assuming a potential $V_c+V_{x\alpha}$. Solve the differential equations and find the spin-
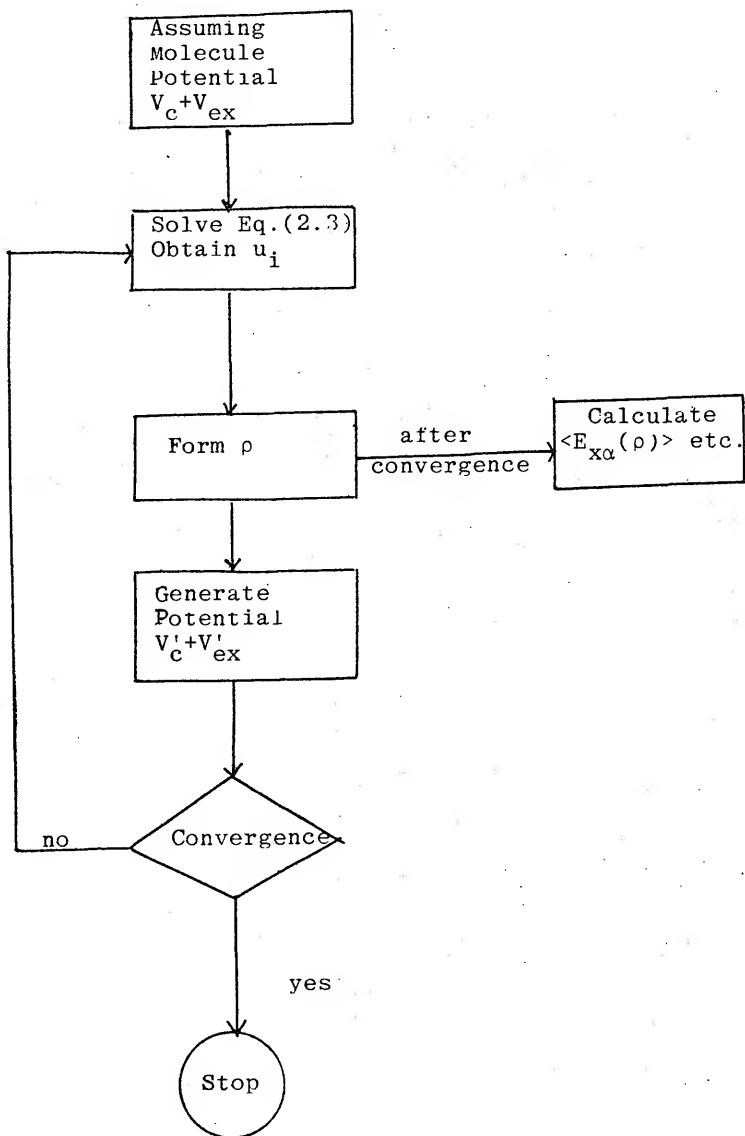
Fig. 2.1 Flow Chart of the Conceptual Exact Xα Method

orbitals. From these spin-orbitals we form the charge densi-
ty. Then, by equations (2.4) and (2.5), we calculate the
potential $V_c'+V_{x\alpha}'$, which is then compared with the starting
potential $V_c+V_{x\alpha}$. If they are "almost" equal to each other,
the calculation is said to have converged. Otherwise we start
with $V_c'+V_{x\alpha}'$ and repeat the cycle again until convergence is
achieved. Then we obtain the spin-orbitals u_i, and with
equation (2.1) we calculate the total energy $<E_{x\alpha}>$. The
conceptual computational scheme is shown in figure (2.1).

There are some difficulties in this scheme, namely:

(1) There is a parameter α in equation (2.2). In
atomic systems, the α value can be chosen in several ways,
all of which amount to almost the same total energy (see
Lindgren and Schwarz(1972)). One of them is to set the α
value such that the total energy calculated be equal to
the exact Hartree-Fock total energy. Another is to set the α
value such that the Hartree-Fock total energy calculated
with the Xα orbitals is a minimum. Still another is to set
the α value such that the virial theorem is satisfied.
However, for molecular systems, the space may not be as
homogeneous as that of the atomic systems, and we need
some other prescriptions to determine the α value.

(2) In general, the potential is a very structured
function. For atomic systems, the potential is spherically
symmetric and it is possible to separate the solutions in
spherical coordinates. However, for molecular systems, the

differential equations usually cannot be separated in any coordinates, unless some approximations are made in the form of the potential.·

(3) Suppose the differential equations are solved and the spin-orbitals are obtained, we still have to calculate the potential by equations (2.4) and (2.5). and to evaluate the total energy by equation (2.1). All of these involve three- and six- dimensional integrals with complicated integrands.

Due to all these difficulties, the MSXα method is suggested. With the muffin-tin approximation and the multiple scattering formalism, the differential equations can be solved easily and the expressions for the total energy and the potential become much more simple. We shall discuss these in the next section.

2.3 Muffin-Tin Approximate Xα One-Electron Equations and the Solutions

The Multiple-Scattering Xα method (MSXα) was suggested by Slater in 1965 and its implementation was begun by Johnson in 1966. There are three basic characteristics in the MSXα method: the exchange-correlation approximation, the muffin-tin approximation for the charge density and the potential, and the multiple scattering formalism.

First, we divide the coordinate space of a molecule into three regions: (I) the contiguous spherical regions surrounding the different nuclei, (II) an intersphere region

which is outside of the spheres of region(I) but inside
region (III), which is the exterior of a sphere enclosing
all the spheres in region (I). The muffin-tin approximation
is such that we approximate the potential and the charge
density in region (I) and region (III) by a spherical aver-
age, and those in region (II) by a volume average, namely:

$$\breve{f}(\vec{r}) = \begin{cases} \overline{f}(r) = \frac{1}{4\pi} \int f(\vec{r})d\Omega & \text{if } \vec{r}\varepsilon \text{ I or III} \\ \\ \overline{f} = \frac{1}{V_{II}} \int_{II} f(\vec{r})d\vec{r} & \text{if } \vec{r}\varepsilon \text{ II} \end{cases}$$

where f is the potential or the charge density function,
V_{II} is the volume of the intersphere region, and $\overline{f}(r)$
is the averaged quantity.

  With the muffin-tin approximation, it can be shown
that the difficulties mentioned in the previous section
can be solved, namely: the differential equations for the
spin-orbitals are separable, the potential can be computed
easily, and the calculation of the total energy reduces to
the evaluation of one-dimensional integrals.

  Starting with the muffin-tin charge density $\overline{\rho}(\vec{r})$,
we have an expression for the approximate $X\alpha$ total energy:

$$\overline{\langle E_{x\alpha} \rangle} = \sum_i n_i \int \breve{u}_i^*(\vec{r})(-\nabla^2)\breve{u}_i(\vec{r})d\vec{r} + U_{NN} + \overline{U}_T$$

where $\breve{u}_i$ are the spin-orbitals that minimize $\overline{\langle E_{x\alpha} \rangle}$,

  U_{NN} is the nuclear-nuclear interaction energy,

  $\overline{U}_T$ is the sum of the nuclear-electron coulomb energy,
electron-electron coulomb energy and the exchange-correlation

energy:

$$\overline{U}_T = \int (\sum_{p=1}^{N} \frac{-2Z_p}{|\vec{r}_1 - \vec{R}_p|})\overline{\rho}(\vec{r}_1)d\vec{r}_1$$

$$+ C_\alpha \int (\overline{\rho}_\uparrow(\vec{r}_1)^{4/3} + \overline{\rho}_\downarrow(\vec{r}_1)^{4/3})d\vec{r}_1$$

$$+ \frac{1}{2} \int d\vec{r}_1 \overline{\rho}(\vec{r}_1) \int d\vec{r}_2 \frac{2\overline{\rho}(\vec{r}_2)}{r_{12}}$$

$$C_\alpha = -\frac{9}{2}\alpha(3/4\pi)^{1/3}$$

With this expression for the total energy, it is shown in Appendix A that the necessary and sufficient condition for $\overline{<E_{x\alpha}>}$ be a minimum is that the $\tilde{u}_i$ satisfy the following differential equations:

$$\{-\nabla^2 + \overline{V}_c(\overline{\rho},\vec{r}) + \overline{V}_{ex}(\vec{r})\} \tilde{u}_i(\vec{r}) = \tilde{\varepsilon}_i \tilde{u}_i(\vec{r}) \qquad (2.6)$$

where $\overline{V}_c(\overline{\rho},\vec{r})$ and $\overline{V}_{ex}(\overline{\rho},\vec{r})$ are the muffin-tin average of $V_c(\overline{\rho},\vec{r})$ and $V_{ex}(\overline{\rho},\vec{r})$ as defined in equations (2.4) and (2.5).

We want to emphasize that the muffin-tin approximate one-electron equations (2.6) are derived from the fact that the charge density is of muffin-tin form. There is only one approximation (besides the Xα exchange-correlation approximation) involved in this derivation, and that is the muffin-tin charge density approximation.

To solve the muffin-tin approximate Xα one-electron equations:

$$\{ -\nabla^2 + \overline{V}_{x\alpha}(\overline{\rho},\vec{r}) \} \tilde{u}_i(\vec{r}) = \tilde{\varepsilon}_i \tilde{u}_i(\vec{r})$$

where we write $\overline{V}_c(\overline{\rho},\vec{r})+\overline{V}_{ex}(\vec{r})$ as $\overline{V}_{x\alpha}(\overline{\rho},\vec{r})$, we may use the partial wave expansions of multiple scattering theory in the different regions of the molecule. Within an atomic sphere β (including the outer sphere which we call the 0th sphere), the potential is spherically symmetric. Thus, we may expand $\tilde{u}_i$ for state i into a linear combination of products of a radial function and a spherical harmonic (here we use the real spherical harmonics for computational convenience):

$$\tilde{u}_i(\vec{r}_\beta) = \sum_{\ell,m} C^{i\beta}_{\ell m} R_\ell(r_\beta,\tilde{\varepsilon}_i) Y^m_\ell(\vec{r}_\beta)$$

where $C^{i\beta}_{\ell m}$ are expansion coefficients to be determined, and the radial functions $R_\ell(r_\beta,\tilde{\varepsilon}_i)$ have to satisfy the following differential equations:

$$\{- \frac{1}{r_\beta^2} \frac{d}{dr_\beta}(r_\beta^2 \frac{d}{dr_\beta}) + \frac{\ell(\ell+1)}{r_\beta^2} + \overline{V}_{x\alpha}(\overline{\rho},r_\beta)\} R_\ell(r_\beta,\tilde{\varepsilon}_i)$$
$$= \tilde{\varepsilon}_i R_\ell(r_\beta,\tilde{\varepsilon}_i)$$

In the intersphere region, the potential is a constant, $\overline{V}_{II}$, and the differential equation for $\tilde{u}_i$ in this region is:

$$\{ - \nabla^2 + (\overline{V}_{II} - \tilde{\varepsilon}_i)\} \tilde{u}_i(\vec{r}) = 0$$

which is just the equation of a free electron. Hence we may express $\tilde{u}_i$ as a multicenter partial wave expansion:

$$
\tilde{u}_i(\vec{r}) = \begin{cases} \displaystyle\sum_{\beta=1}^{N} \sum_{\ell,m} A_{\ell m}^{i\beta}\; \eta_\ell(\kappa_i r_\beta) Y_\ell^m(\vec{r}_\beta) + \sum_{\ell,m} A_{\ell m}^{i0}\; j_\ell(\kappa_i r_0) Y_\ell^m(\vec{r}_0) \\ \qquad\qquad\qquad\qquad\qquad\qquad \text{if}\quad \tilde{\epsilon}_i > \overline{V}_{II} \\[4pt] \displaystyle\sum_{\beta=1}^{N} \sum_{\ell,m} A_{\ell m}^{i\beta}\; k_\ell(\kappa_i r_\beta) Y_\ell^m(\vec{r}_\beta) + \sum_{\ell,m} A_{\ell m}^{i0}\; i_\ell(\kappa_i r_0) Y_\ell^m(\vec{r}_0) \\ \qquad\qquad\qquad\qquad\qquad\qquad \text{if}\quad \tilde{\epsilon}_i < \overline{V}_{II} \end{cases}
$$

where $\kappa_i = (|\overline{V}_{II} - \tilde{\epsilon}_i|)^{\frac{1}{2}}$,

η_ℓ is the ordinary Neumann function,

j_ℓ is the ordinary Bessel function,

k_ℓ is the modified spherical Hankel function of the
first kind,

i_ℓ is the modified spherical Bessel function,

and $A_{\ell m}^{i\beta}$ are the expansion coefficients to be determined.

With the requirements that the spin-orbitals $\tilde{u}_i$ and
their derivatives have to be continuous on the boundaries of
the spheres, we obtain a secular equation from which the
eigenvalues $\tilde{\epsilon}_i$ and the expansion coefficients { $C_{\ell m}^{i\beta}$ } and
{ $A_{\ell m}^{i\beta}$ } can be determined. Appendix **B** gives the details
of the procedure to determine the eigenvalues and the expan-
sion coefficients.

2.4 Relation Between the Exact Xα Method
and the Muffin-Tin Approximate Xα Method

In this section, we shall discuss the relation
between the exact Xα spin-orbitals u_i and the spin-orbitals
$\tilde{u}_i$ derived from the muffin-tin approximate one-electron
equation (henceforth called MSXα spin-orbitals). First of

Fig. 2,2 Flow Chart of the Conceptual Exact
          Xα Method and the MSXα Method.

          ------> Exact Xα
          ——————> MSXα
          —·—·—·→ Non-Muffin-Tin Calculation

Superimposing atomic Xα pot to form $V_{x\alpha}$

MT $\bar{V}_{x\alpha}$

Solve exact Xα eq. to obtain u_i

Solve MT eq. to obtain $\tilde{u}_1$

Calc. $\langle E_{x\alpha}(\rho)\rangle$ $F(\rho)$, $\mu(\rho)$

after converg.

Form ρ

Form $\tilde{\rho}$

after converg.

Calc. $\langle E_{x\alpha}(\tilde{\rho})\rangle$ $F(\tilde{\rho})$, $\mu(\tilde{\rho})$

MT $\bar{\rho}$

after converg.

Calc. $\langle E_{x\alpha}(\bar{\rho})\rangle$ $F(\bar{\rho})$, $\mu(\bar{\rho})$

Generate $V_{x\alpha}(\rho)$

Generate $V_{x\alpha}(\bar{\rho})$

MT $\bar{V}_{x\alpha}(\bar{\rho})$

no

no

Convergence

Convergence

yes

yes

Stop

Stop

all, we shall look at the differences between the two self-consistent cycles for the conceptual exact $X\alpha$ method and the muffin-tin approximate $X\alpha$ method (figure 2.2).

Both SCF cycles start with the superposition of atomic potentials. In the exact $X\alpha$ method we try to solve the Schrödinger equations (2.3) to get u_i directly from this potential whereas in the MSXα method we solve the Schrödinger equations (2.6) to get $\tilde{u}_i$ after the potential being muffin-tin averaged. Then the charge density ρ is formed from either u_i or $\tilde{u}_i$. In the exact $X\alpha$ method the potential is formed from ρ while in the MSXα method the potential is formed from the muffin-tin part of the charge density, namely $\bar{\rho}$. Then we repeat the cycle again until the convergence is achieved. Then the total energy is computed with ρ or $\bar{\rho}$ as the charge density respectively in the exact $X\alpha$ method and the MSXα method.

As we have mentioned in the previous sections, the basic difference between the exact $X\alpha$ spin-orbitals u_i and the MSXα spin-orbitals $\tilde{u}_i$ is that they minimize two different total energy functionals, $<E_{X\alpha}(\rho)>$ and $\overline{<E_{X\alpha}(\bar{\rho})>}$. In other words, we have two different hamiltonians: H, the hamiltonian for the exact $X\alpha$ method, and $\overline{H}$, the hamiltonian for the MSXα method. The u_i and $\tilde{u}_i$ are the eigenfunctions of H and $\overline{H}$ respectively.

Since we had employed the approximate hamiltonian in our calculations, an important question should arise:

how is the quality of the MSXα spin-orbtials $\tilde{u}_i$, or how good are they compared to the exact Xα spin-orbitals u_i? The calculations of the non-muffin-tin total energy by using the MSXα spin-orbitals $\tilde{u}_i$ done by Danese (see Danese(1973)) have given part of the answer to this question (we shall give a more detailed discussion about this calculation in the next chapter). In this dissertation, we want to look at the quality of $\tilde{u}_i$ in two more aspects: the Hellmann-Feynman force and the dipole moment calculations.

It was proved by Slater that the exact Xα spin-orbitals (with the restriction that the α parameter be a constant) satisfy the Hellmann-Feynman Theorem. That is, the electrostatic force calculated with u_i should be equal to the derivative of the quantum mechanical expectation value of the hamiltonian H with respect to the coordinate of the nucleus upon which the force is exerted. Now, instead of u_i, we have $\tilde{u}_i$; and instead of the exact Xα total energy $\langle E_{x\alpha}(\rho) \rangle$, we have the non-muffin-tin total energy $\langle E_{x\alpha}(\tilde{\rho}) \rangle$. We can check if the $\tilde{u}_i$ satisfy the Hellmann-Feynman Theorem and test their quality.

Also, dipole moment calculations are performed on some diatomic molecules by using $\tilde{u}_i$ as the wavefunctions. As we know, the dipole moment is much more sensitive to the wavefunction than the energy is. Therefore, the dipole moment calculations should be a good check on the quality of the spin-orbitals too.

Since we do have some reasonable results for the total energy by assuming the muffin-tin charge density $\bar{\rho}$, we wonder what would be the result if we assume the same kind of approximation in the force and dipole moment calculations. So, before we discuss the force and dipole moment calculations by using the MSXα spin-orbitals $\tilde{u}_i$, we shall first investigate these two kinds of calculations by assuming the muffin-tin charge density $\bar{\rho}$ in the next chapter. We shall see that the results are not satisfactory and hence it is necessary to use the $\overset{\sim}{\rho}$ formed from $\tilde{u}_i$, instead of the crude approximation $\bar{\rho}$, in such calculations. The distinction between these two different approaches is also shown in figure (2.2).

CHAPTER III

MUFFIN-TIN CHARGE DENSITY APPROXIMATION

3.1 Introduction

In the last chapter, we discussed the exact Xα
one-electron equation. Instead of solving this exact equa-
tion, we solve the muffin-tin approximate Xα one-electron
equation which is obtained by varying the Xα total energy
functional by assuming a muffin-tin charge density approxi-
mation. Since we had assumed this approximation, we would
like to see how good it is. One way to check the validity
of the muffin-tin charge density approximation is to look
at some of the molecular property calculations using the
muffin-tin averaged charge density. In this chapter, we
shall discuss three such calculations: the total energy
calculations, the electrostatic force calculations and
the dipole moment calculations. With the results obtained,
we conclude that in most cases it is not satisfactory to
use the muffin-tin charge density in the molecular calcula-
tions. Also, we shall discuss the non-muffin-tin total
energy calculations done by Danese. With the success of
his calculations, it seems that we should use the charge
density generated by the spin-orbitals $\tilde{u}_i$, rather than the

muffin-tin charge density, in the molecular property calculations.

3.2 Muffin-Tin Xα Total Energy Calculations

As we have shown in the last chapter, we calculate the Xα total energy by using the muffin-tin charge density. In solid state systems, especially the close-packed system, the use of the muffin-tin approximation is usually quite successful. However, for molecular systems, it is not uniformly good. Although the absolute values of the total energy are quite close to the experimental results, we have some bad results when we consider the dissociation energy and the conformation of the systems. The calculation by Connolly and Sabin(see Connolly and Sabin(1972)) on the water molecule led to a minimum total energy for a linear molecule rather than for the bent form known to be correct experimentally. The work in many diatomic molecules indicates no binding too.

It is noticed that the results are worse in loose-packed systems than in close-packed systems. It was suggested that this is because the intersphere region is larger in the previous case than in the latter case, and the muffin-tin effect is correspondingly more severe. This was verified by the work done by Danese and Connolly. Danese performed the calculations for the non-muffin-tin Xα total energy of carbon and neon molecule by using the MSXα spin-orbitals

rather than the muffin-tin charge density (see Danese
(1973)). The result is dramatically improved for C_2. One
finds binding very much closer to the experimental value
than in Hartree-Fock calculation, and somewhat closer than
the result of the configuration interaction calculation.
For Ne_2, one also finds binding.

    With the calculations on the total energy, one may
conclude that the approximation of charge density has quite
a large effect on the molecular properties. In the later
sections, we shall show such muffin-tin charge density effect
on the electrostatic force and the dipole moments.

3.3 Force Calculations

    In the last section, we have shown that the use of
MSXα spin-orbitals $\tilde{u}_i$ causes a big improvement in the total
energy calculations. In this section, we shall look at $\tilde{u}_i$
in a more elaborate way.

    As we know, the error in the total energy calcula-
tion is of second order in the error in the wavefunction.
We would like to look at some molecular properties which
are more sensitive to the wavefunction. The force exerted
on a nucleus by the electronic charge cloud and the other
nuclei is a good test of the quality of the wavefunctions.
The Hellmann-Feynman Theorem, which we shall discuss in
more detail in the next chapter, provides a way to calculate
this force. It was proved (see Slater(1972b)) that this

theorem holds for exact Xα spin-orbitals u_i (with the restriction that the α parameter be a constant). However, it is well known that for approximate wavefunctions the theorem often gives rather unreliable results. Thus, it should be a good test of the MSXα spin-orbitals by employing them in a calculation of the force exerted on a nucleus of a molecule by means of the Hellmann-Feynman Theorem.

We shall discuss such a calculation in Chapter IV. Before that, we may wonder what the result would be if we use the muffin-tin charge density in such a calculation, just as in the total energy calculation. We shall show in the following that for homonuclear diatomic molecules, the force obtained with such a muffin-tin approximation would be always be repulsive. This cannot be physically possible because that would mean there is no binding for such a system.

In the MSXα calculation of a homonuclear diatomic molecule, the space is partitioned into three regions: two atomic spheres surrounding the two nuclei A and B, each with nuclear charge Z, an outer sphere enclosing the two atomic spheres, and the intersphere region II, as shown in figure (3.1).

By symmetry, the force on nucleus A is along the z-axis and is given by:

$$F_A = 2Z \int \frac{\rho(\vec{r}) \cos\theta_A}{r_A^2} d^3r - \frac{2 Z}{R_{AB}^2} \qquad (3.1)$$
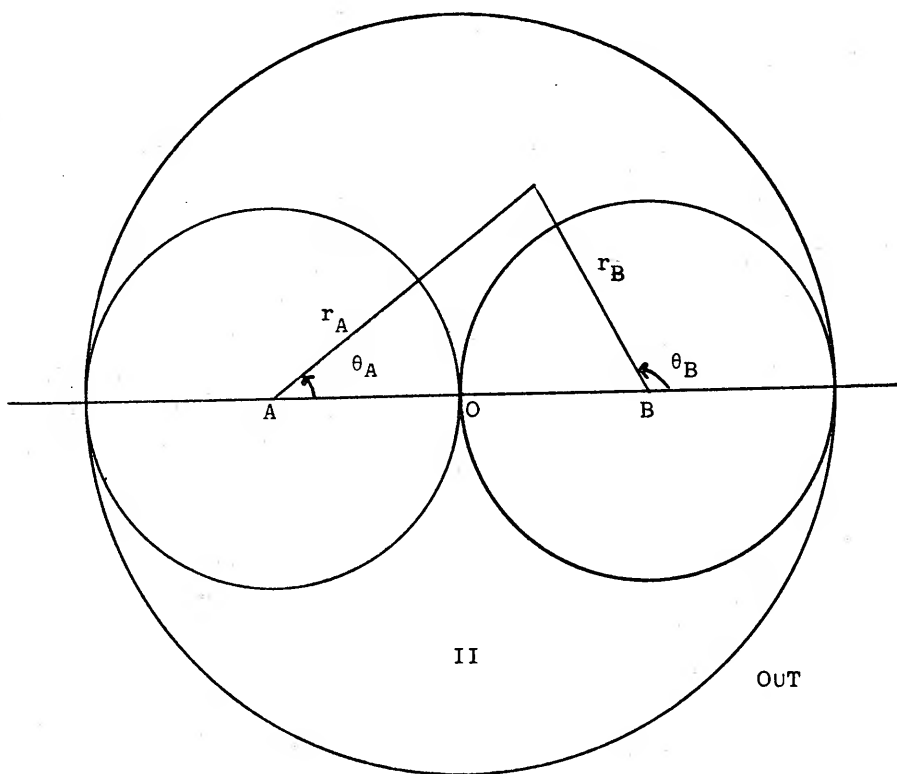
Fig. 3.1   Partitioning of the Space of a Homonuclear
Diatomic Molecule in the MSXα Method.

where ρ is the charge density in atomic unit,

Θ_A is the azimuthal angle measured with nucleus A at the center,

r_A is the distance from nucleus A,

R_{AB} is the separation of the two nuclei,

F_A is in Rydberg/a.u. units.

Now, if the muffin-tin charge density approximation is assumed, the quantity ρ in equation (3.1) will be replaced by $\bar{\rho}$ and the calculation for F_A becomes much more simple. First, we decompose the integral into four different parts, one over each region:

$$\int \frac{\bar{\rho}(\vec{r}) \cos\Theta_A}{r_A^2} d^3r = I_A + I_B + I_{out} + I_{II}$$

where

$$I_A = \int_A \frac{\bar{\rho}(\vec{r}) \cos\Theta_A}{r_A^2} d^3r$$

$$I_B = \int_B \frac{\bar{\rho}(\vec{r}) \cos\Theta_A}{r_A^2} d^3r$$

$$I_{out} = \int_{out} \frac{\bar{\rho}(\vec{r}) \cos\Theta_A}{r_A^2} d^3r$$

$$I_{II} = \int_{II} \frac{\bar{\rho}(\vec{r}) \cos\Theta_A}{r_A^2} d^3r$$

We shall discuss each of the above integrals in the following:

Integral Over Sphere A: I_A

Since $\bar{\rho}(\vec{r})$ is spherically symmetric inside sphere A,

we have:

$$I_A = \int_A \frac{\bar{\rho}(\vec{r}) \cos\Theta_A}{r_A^2} d^3r$$

$$= \int_0^{R_A} \frac{\bar{\rho}(r_A)}{r_A^2} r_A dr_A \int_0^\pi \cos\Theta_A \sin\Theta_A d\Theta_A \int_0^{2\pi} d\phi_A$$

where R_A is the radius of the sphere A and is equal to one half of the separation of the bond distance R.

Since the integral over the coordinate Θ_A is equal to zero, we have $I_A = 0$.

Integral Over Sphere B: I_B

To evaluate the other integrals, we need to expand $\frac{\cos\Theta_A}{r_A^2}$ in terms of functions centered at nucleus B or at the center of the outer sphere. Such an expression can be derived from an expansion theorem for Neumann functions (see Appenix F). The expression is as follows:

$$\frac{Y_1^0(\vec{r}_A)}{r_A^2} = \begin{cases} -4\pi \displaystyle\sum_{\ell=0}^\infty I(\ell+1,0;1,0;\ell,0) \frac{Y_{\ell+1}^0(\vec{R}_A-\vec{R}_B)}{R_{AB}^{\ell+1}} r_B^\ell Y_\ell^0(\vec{r}_B) \\ \qquad\qquad\qquad \text{(if } r_B < R_{AB}) \qquad\qquad (3.2) \\ 4\pi \displaystyle\sum_{\ell=1}^\infty I(\ell-1,0;1,0;\ell,0) R_{AO}^{\ell-1} Y_{\ell-1}^0(\vec{R}_A-\vec{R}_B) \frac{Y_\ell^0(\vec{r}_0)}{r_0^{\ell+1}} \\ \qquad\qquad\qquad \text{(if } r_0 > R_{AO}) \qquad\qquad (3.3) \end{cases}$$

where Y_ℓ^m are the real spherical harmonics,

$I(\ell_1,m_1;\ell_2,m_2;\ell_3,m_3)$ are the Gaunt coefficients for real spherical harmonics and are defined by:

$$\int Y_{\ell_1}^{m_1}(r) Y_{\ell_2}^{m_2}(r) Y_{\ell_3}^{m_3}(r) d\Omega \qquad , \qquad (3.4)$$

and R_{AB}, R_{A0} are the distances between A and B and between A and O respectively.

Inside sphere B, we have $r_B < R_{AB}$ and we can use equation (3.2) for the evaluation of I_B:

$$I_B = \int_B \frac{\bar{\rho}(\vec{r}) \cos\Theta_A}{r_A^2} d^3r$$

$$= \int_B \bar{\rho}(\vec{r}) (4\pi/3)^{\frac{1}{2}} \frac{Y_1^0(\vec{r}_A)}{r_A^2} d^3r$$

$$= (4\pi/3)^{\frac{1}{2}} \int_B \bar{\rho}(r_B)(-4\pi) \sum_{\ell=0}^{\infty} I(\ell+1,0;1,0;\ell,0)$$

$$\times \frac{Y_{\ell+1}(\vec{R}_A-\vec{R}_B)}{R_{AB}^{\ell+2}} r_B^{\ell} Y_\ell^0(\vec{r}_B) d^3r$$

$$= (4\pi/3)^{\frac{1}{2}}(-4\pi) \sum_{\ell=0}^{\infty} I(\ell+1,0;1,0;\ell,0) \frac{Y_{\ell+1}^0(\vec{R}_A-\vec{R}_B)}{R_{AB}^{\ell+2}}$$

$$\times \int_0^{R_B} \bar{\rho}(r_B) r_B^{\ell+2} dr_B \int Y_\ell^0(\vec{r}_B) d\Omega_B$$

$$\because \int Y_\ell^0(\vec{r}_B) d\Omega_B = (4\pi)^{\frac{1}{2}} \delta_{\ell 0}$$

$$\therefore I_B = (4\pi/3)^{\frac{1}{2}} (-4\pi) I(1,0;1,0;0,0) \frac{Y_1^0(\vec{R}_A-\vec{R}_B)}{R_{AB}^2}$$

$$\times (4\pi)^{\frac{1}{2}} \int_0^{R_B} \bar{\rho}(r_B) r_B^2 dr_B$$

Since $I(1,0;1,0;0,0)=(1/4\pi)^{\frac{1}{2}}$
and $Y_1^0(\vec{R}_A-\vec{R}_B) = Y_1^0(\Theta_A = \pi) = (3/4\pi)^{\frac{1}{2}}\cos\pi = -(3/4\pi)^{\frac{1}{2}}$

therefore $I_B = \dfrac{1}{R_{AB}^2} \displaystyle\int_o^{R_B} \overline{\rho}(r_B) 4\pi r_B^2 \, dr_B = Q_B / R_{AB}^2$

where $Q_B = \displaystyle\int_o^{R_B} \overline{\rho}(r_B) 4\pi \, r_B^2 \, dr_B$ is the electronic charge

inside sphere B.

<u>Integral Over the Outer Sphere</u>: I_{out}

        In the outer sphere, $r_0 > R_{A0}$, so we can use equation

(3.3) for the expansion of $\dfrac{\cos\Theta_A}{r_A^2}$. Then we have:

$$I_{out} = \int_{out} \overline{\rho}(\vec{r}) \frac{\cos\Theta_A}{r_A^2} \, d^3r$$

$$= (4\pi/3)^{\frac{1}{2}} \int_{out} \overline{\rho}(r_0) 4\pi \sum_{\ell=1}^{\infty} I(\ell-1,0;1,0;\ell,0)$$

$$\times \ R_{A0}^{\ell-1} \ Y_{\ell-1}^{0}(\vec{R}_A - \vec{R}_0) \ \frac{Y_{\ell}^{0}(\vec{r}_0)}{r_0^{\ell+1}} \ d^3r$$

$$= \ 4\pi(4\pi/3)^{\frac{1}{2}} \sum_{\ell=1}^{\infty} I(\ell-1,0;1,0;\ell,0) \ R_{A0}^{\ell-1} \ Y_{\ell-1}^{0}(\vec{R}_A - \vec{R}_0)$$

$$\times \int_{R_{out}}^{\infty} \frac{\overline{\rho}(r_0)}{r_0^{\ell+1}} \ r_0^2 \, dr_0 \int Y_{\ell}^{0}(\vec{r}_0) \ d\Omega_0$$

Since $\displaystyle\int Y_{\ell}^{0}(\vec{r}_0) \ d\Omega_0 = (4\pi)^{\frac{1}{2}} \delta_{\ell 0}$,

and $\ell \neq 0$ in the summation, therefore $I_{out} = 0$

<u>Integral Over the Intersphere Region</u>: I_{II}

        In the intersphere region, the muffin-tin charge

density is a constant, so we can take $\overline{\rho}$ out of the integral:

$$I_{II} = \int_{II} \frac{\bar{\rho}(\vec{r})\,\cos\Theta_A}{r_A^2}\,d^3r = \bar{\rho}_{II}\int_{II}\frac{\cos\Theta_A}{r_A^2}\,d^3r$$

We further decompose the integral into three parts:

$$\int_{II}\frac{\cos\Theta_A}{r_A^2}\,d^3r = \int_{A+B+II}\frac{\cos\Theta_A}{r_A^2}\,d^3r - \int_A\frac{\cos\Theta_A}{r_A^2}\,d^3r$$

$$- \int_B\frac{\cos\Theta_A}{r_A^2}\,d^3r$$

Just as for I_A and I_B, we have:

$$\int_A\frac{\cos\Theta_A}{r_A^2}\,d^3r = 0$$

and

$$\int_B\frac{\cos\Theta_A}{r_A^2}\,d^3r = (\int_0^{R_B}4\pi r_B^2\,dr_B)/R_{AB}^2 = \pi R_{AB}/6$$

For the first term, we have:

$$\int_{A+B+II}\frac{\cos\Theta_A}{r_A^2}\,d^3r$$

$$= (4\pi/3)^{\frac{1}{2}}\,\{\int_{0\leq r_0\leq R_{AO}}\frac{Y_1^0(\vec{r}_A)}{r_A^2}\,d^3r + \int_{R_{AO}\leq r_0\leq R_{AB}}\frac{Y_1^0(\vec{r}_A)}{r_A^2}\,d^3r\,\}$$

$$= (4\pi/3)^{\frac{1}{2}}\,\{(-4\pi)\sum_{\ell=0}^{\infty}I(\ell+1,0;1,0;\ell,0)\,\frac{Y_\ell^0(\vec{R}_A-\vec{R}_0)}{R_{AO}^{\ell+2}}$$

$$\times \int_0^{R_{AO}}r_0^{\ell+2}\,dr_0\int Y_\ell^0(\vec{r}_0)\,d\Omega_0$$

$$+4\pi\sum_{\ell=1}^{\infty}I(\ell-1,0;1,0;\ell,0)\,R_{AO}^{\ell-1}Y_{\ell-1}^0(\vec{R}_A-\vec{R}_0)$$

$$\times \int_{R_{AO}}^{R_{AB}} r_0^2 \; \frac{1}{r_0^{\ell-1}} \; dr_0 \quad \int Y_\ell^0(\vec{r}_0)d\Omega_0 \}$$

$$= 4\pi R_{AO}/3 = 2\pi R_{AB}/3$$

Putting all of them together:

$$I_{II} = \overline{\rho}_{II} \; (\; 2\pi R_{AB}/3 \; - \; \pi R_{AB}/6 \;) = \overline{\rho} \; \pi R_{AB}/2$$

We can express $\overline{\rho}_{II}$ in terms of the total charge Q_{II} in the intersphere region and the volume V_{II}:

$$V_{II} = (4\pi/3) \; (R_{AB}^3 \; - \; R_A^3 \; - \; R_B^3) = \pi R_{AB}^3$$

Therefore $\quad I_{II} = \dfrac{Q_{II}}{V_{II}} \; \pi \; R_{AB}/2 = \dfrac{Q_{II}}{2 \; R_{AB}^2}$

Combining $I_A, I_B, I_{out}, \; I_{II}$ and the nucleus force, we have:

$$F_A = 2Z \quad \int \quad \overline{\rho}(r) \; \frac{\cos\Theta_A}{r_A^2} \; d^3r \; - \; 2Z^2/R_{AB}^2$$

$$= 2Z \; (I_A \; + \; I_B \; + \; I_{out} \; + \; I_{II}) \; - \; 2Z^2/R_{AB}^2$$

$$= 2Z \; (0 \; + \; \frac{Q_B}{R_{AB}^2} \; + \; 0 \; + \; \frac{Q_{II}}{2 \; R_{AB}^2}) \; - \; 2Z^2/R_{AB}^2$$

$$= \frac{2Z}{R_{AB}^2} \; (Q_B \; + \; Q_{II}/2 \; - \; Z)$$

Since for a homonuclear diatomic molecule, we have:

$$Q_{II} = Q_{total} \; - \; 2 \; Q_B \; - \; Q_{out}$$

where Q_{out} is the charge in the outer sphere.

Also, for a neutral homonuclear diatomic molecule, $Q_{total}=2Z$. Thus, we finally have:

$$F_A = \frac{2Z}{R_{AB}^2} (Q_B + Q_{total}/2 - Q_B - Q_{out}/2 -Z)$$

$$= \frac{2Z}{R_{AB}^2} (-Q_{out}/2 + Z - Z)$$

$$= -\frac{Z\ Q_{out}}{R_{AB}^2} \tag{3.5}$$

Since Q_{out} is always positive, we have the result that the force exerted on the nucleus A is always negative, or away from the other nucleus. Thus we prove that the force is always repulsive for a homonuclear diatomic molecule if we assume the muffin-tin charge density.

Due to such a result, we see that it is inadequate to employ the muffin-tin charge density approximation in the force calculations. As in the total energy calculations, we hope that improvements may be achieved if we use the charge density $\tilde{\rho}$ generated by the MSXα spin-orbitals, instead of the muffin-tin charge density. Indeed, we have some improvements as we shall discuss in Chapter IV.

3.4 Dipole Moment Calculations

Another way to check the quality of the wavefunctions is to look at the dipole moment calculations. As is well known, the dipole moment is very sensitive to the wavefunc-

tion employed in the calculations. We shall use the MSXα spin-orbitals for such an investigation. Before that, we first derive an expression for the dipole moment calculated from the muffin-tin charge density. We shall see that such a charge density approximation is also inadequate, and we need a more elaborate way to evaluate the dipole moment.

Consider a neutral diatomic molecule AB. We partition the space as we do in the force calculation. Since we have a heteronuclear diatomic molecule, sphere A and sphere B are in general of different size.

The dipole moment is defined as:

$$\vec{\mu} = - \int \overline{\rho}(\vec{r})\vec{r} \, d^3r + \vec{\mu}_N$$

where $\overline{\rho}(\vec{r})$ is the muffin-tin charge density,

$\vec{\mu}_N$ is the nuclear contribution and is defined by:

$$\vec{\mu}_N = Z_A\vec{R}_A + Z_B\vec{R}_B.$$

For a neutral molecule, it can be shown (Appendix D) that the dipole moment is independent of the choice of the origin. Thus, for computational convenience, we can choose the origin at the center of the outer sphere. Furthermore, by the axial symmetry of the system, we note that the only non-vanishing component is the z-component. Thus,

$$\mu = - \int \overline{\rho}(\vec{r})z_0 \, d^3r + \mu_N$$

To evaluate the integral, we decompose it into four parts again:

$$\int \bar{\rho}(\vec{r})z_0 \ d^3r$$

$$= \int_A \bar{\rho}(\vec{r})z_0 d^3r \ + \ \int_B \bar{\rho}(\vec{r})z_0 \ d^3r \ + \ \int_{out} \bar{\rho}(\vec{r})z_0 \ d^3r$$

$$+ \ \int_{II} \bar{\rho}(\vec{r})z_0 \ d^3r$$

We shall consider them one by one:

(1) $\displaystyle\int_A \bar{\rho}(\vec{r})z_0 \ d^3r$

$$= \int_A \bar{\rho}(\vec{r}) \ (r_A \cos\Theta_A - R_{A0}) \ d^3r$$

$$= \int_o^{R_A} \bar{\rho}(r_A)r_A^3 \ dr_A \int \cos\Theta_A \ d\Omega_A \ - \ R_{A0} \int_A \bar{\rho}(\vec{r}) \ d^3r$$

$$= 0 \ - \ R_{A0}Q_A \ = \ - \ R_{A0}Q_A$$

(2) $\displaystyle\int_B \bar{\rho}(\vec{r})z_0 \ d^3r$

$$= \int_B \bar{\rho}(\vec{r}) \ (r_B \cos\Theta_B + R_{B0}) \ d^3r$$

$$= \int_o^{R_B} \bar{\rho}(r_B)r_B^3 \ dr_B \int \cos\Theta_B \ d\Omega_B \ + \ R_{B0} \int_B \bar{\rho}(\vec{r}) \ d^3r$$

$$= 0 \ + \ R_{B0}Q_B \ = \ R_{B0}Q_B$$

(3) $\quad \int_{out} \bar{\rho}(\vec{r})z_0 \, d^3r$

$\quad = \int_{out} \bar{\rho}(r_0)r_0\cos\Theta_0 \, d^3r$

$\quad = \int_{R_{out}}^{\infty} \bar{\rho}(r_0)r_0^3 \, dr_0 \int \cos\Theta_0 \, d\Omega_0 \quad = 0$

(4) $\quad \int_{II} \bar{\rho}(\vec{r})z_0 \, d^3r$

$\quad = \bar{\rho}_{II} \int_{II} z_0 \, d^3r$

$\quad = \bar{\rho}_{II} \left(\int_{A+B+II} z_0 \, d^3r - \int_A z_0 \, d^3r - \int_B z_0 \, d^3r \right)$

$\quad = \bar{\rho}_{II} \left\{ \int_0^{R_{AB}} r_0^3 \, dr_0 \int \cos\Theta_0 \, d\Omega_0 - \int_A (r_A\cos\Theta_A - R_{A0}) \, d^3r \right.$

$\quad \left. - \int_B (r_B\cos_B + R_{B0}) \, d^3r \right\}$

$\quad = \bar{\rho}_{II} \left(0 + R_{A0}V_A - R_{B0}V_B \right)$

where V_A and V_B are the volume of sphere A and sphere B
respectively.

$\qquad$ Combining all the terms, we have:

$\int \bar{\rho}(\vec{r})z_0 \, d^3r = - R_{A0}Q_A + R_{B0}Q_B + \bar{\rho}_{II}(V_A R_{A0} - V_B R_{B0})$

Since $\quad R_{A0} = (R_A + R_B) - R_A = R_B$

$$R_{BO} = (R_A + R_B) - R_B = R_A$$

$$V_A = 4\pi R_A^3/3$$

$$V_B = 4\pi R_B^3/3$$

$$\overline{\rho}_{II} = Q_{II}/V_{II} = Q_{II}/ 4\pi R_A R_B (R_A + R_B)$$

Therefore $\displaystyle\int \overline{\rho}(\vec{r})z_0 \, d^3r$

$$= - R_B Q_A + R_A Q_B + \frac{Q_{II}}{4\pi R_A R_B (R_A + R_B)} \frac{4\pi}{3} (R_A^3 R_B - R_B^3 R_A)$$

$$= - R_B Q_A + R_A Q_B + Q_{II}(R_A - R_B)/3$$

Also, $\quad \mu_N = Z_B R_{BO} - Z_A R_{AO} = Z_B R_A - Z_A R_B$

Thus, finally we have:

$$\mu = - \{- R_B Q_A + R_A Q_B + Q_{II}(R_A - R_B)/3\} + Z_B R_A - Z_A R_B$$

$$= R_B(Q_A + Q_{II}/3 - Z_A) - R_A(Q_B + Q_{II}/3 - Z_B)$$

$$(3.6)$$

We shall discuss the results computed with the above equation in Chapter V. There we shall find that most of the results are not satisfactory when compared with the experimental values or with the results obtained by other methods.

The reason is simple: the expression (3.5) depends entirely on the crude approximation of muffin-tin charge density. We hope that improvements may be achieved by using the charge density generated by the MSXα spin-orbitals instead of the crude muffin-tin density. We shall devote Chapter V to such calculations.

CHAPTER IV

HELLMANN-FEYNMAN FORCE CALCULATIONS

4.1 Introduction

In the last chapter, we saw the necessity of using
the non-muffin-tin charge density generated from the MSXα
spin-orbitals $\tilde{u}_i$ in the force and dipole moment calculations.
To carry out these calculations, we need to evaluate a three-
dimensional integral whose integrand is a multi-center func-
tion. The basic difficulty of such calculations is the eval-
uation of the integral over the intersphere region, which is
in general very awkward. In this chapter, we shall develop
an analytical way to perform such integrals for the case of
diatomic molecules, and we shall apply it to the force calcu-
lations.

4.2 Prolate Spheroidal Coordinates

Before we go into the force and dipole moment calcu-
lations, we first introduce the Prolate Spheroidal Coordinates
that are essential to our scheme of evaluating the integral
over the intersphere region.

Let A and B, with separation of R, be the two foci
of our coordinates. Also, let (r_A, θ_A, ϕ_A) and (r_B, θ_B, ϕ_B)
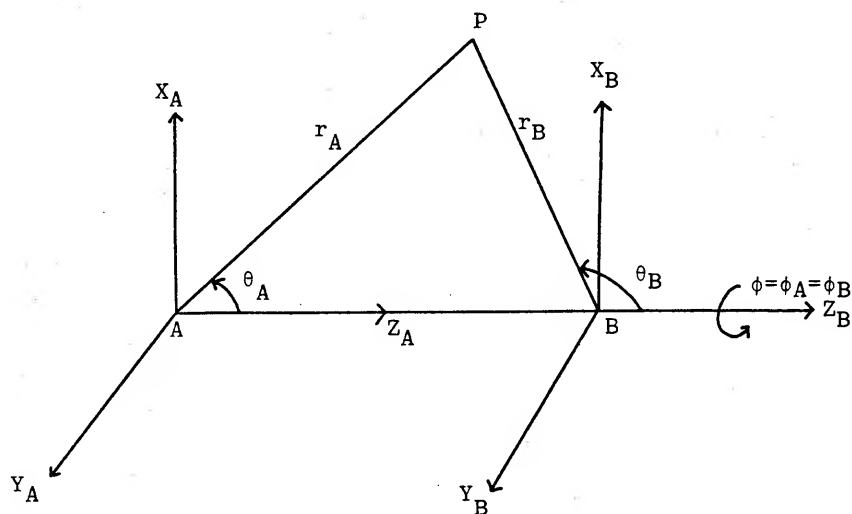
Fig. 4.1   Representation of a Point in the Atomic Coordinates.

be the two spherical coordinates with centers located at A and B respectively. Θ_A and Θ_B are both measured from the major axis in the same direction, as shown in figure (4.1). The Prolate Spheroidal Coordinates are defined as:

$$\xi = (r_A + r_B)/R$$

$$\eta = (r_A + r_B)/R \qquad\qquad (4.1)$$

$$\phi = \phi_A = \phi_B$$

The reciprocal relations are:

$$r_A = R(\xi + \eta)/2 \qquad\qquad\qquad r_B = R(\xi - \eta)/2$$

$$\cos\Theta_A = (1 + \xi\eta)/(\xi + \eta) \quad\text{and}\quad \cos\Theta_B = -(1 - \xi\eta)/(\xi - \eta)$$

$$\sin\Theta_A = \frac{\{(\xi^2 - 1)(1 - \eta^2)\}^{\frac{1}{2}}}{\xi + \eta} \qquad\qquad \sin\Theta_B = \frac{\{(\xi^2 - 1)(1 - \eta^2)\}^{\frac{1}{2}}}{\xi - \eta}$$

$$(4.2)$$

Also, it can be shown that the volume element is:

$$d^3r = (R/2)^3(\xi^2 - \eta^2)\, d\xi\, d\eta\, d\phi \qquad\qquad (4.3)$$

If the integral is over the entire space, the integration limits would be: $1 \leqslant \xi < \infty$, $-1 \leqslant \eta \leqslant 1$, and $0 \leqslant \phi \leqslant 2\pi$. However, if we are evaluating an integral over a finite space

only, such as the integral over the intersphere region, the
integration limits have to be modified. We shall use the two
atomic centers or one atomic center together with the center
of the outer sphere as the two foci, depending on the form
of the integrands, in our treatment of the integrals.

4.3 Hellmann-Feynman Theorem

It was proved (see Slater (1972b)) that the exact Xα
spin-orbitals, with the restriction that the α value be a
constant everywhere, rigorously obey the Hellmann-Feynman
Theorem. In other words, the force component $-\frac{\partial <E_{X\alpha}>}{\partial X_p}$
acting on a nuclear coordinate X_p, where $<E_{X\alpha}>$ is the exact
Xα total energy of the system as calculated quantum-mechani-
cally from the exact Xα spin-orbitals, is the force which
would be calculated by pure classical electrostatics acting
on this nuclear coordinate, resulting from the electronic
charge cloud, formed by the exact Xα spin-orbitals, and all
other nuclei. We can express the theorem in the following
form:

$$-\frac{\partial <E_{X\alpha}>}{\partial X_p} = \int \rho_{X\alpha}(\vec{r}) \frac{\partial}{\partial X_p}(\frac{2Z_p}{|\vec{r}-\vec{R}_p|}) d^3r - \sum_{\ell \neq p} \frac{\partial}{\partial X_p}(\frac{2Z_p Z_q}{|\vec{R}_p-\vec{R}_q|})$$

$$(4.4)$$

where Z_p is the atomic number of the pth nucleus,

$<E_{X\alpha}>$ is the exact Xα total energy in Rydberg units,

$\rho_{X\alpha}$ is the electronic charge density formed by the
exact Xα spin-orbitals,

$\vec{R}_p$, $\vec{R}_q$ are the nuclear coordinates.

In the above theorem, we want to emphasize that the spin-orbitals and the total energy are those derived from the exact Xα method. As we have mentioned in the previous chapters, the existing MSXα calculations are not exact Xα calculations. They assume the muffin-tin approximation. With such an approximation, we can ask the following two questions:

(1) Does the Hellmann-Feynman Theorem hold for the approximate Xα spin-orbitals $\tilde{u}_i$? If not, then how severe is the discrepancy? In other words, we want to see how large is the difference between $-\frac{\partial \overline{<E_{x\alpha}>}}{\partial X_p}$ and $F_p(\tilde{\rho}_{x\alpha})$, where $\overline{<E_{x\alpha}>}$ is the Xα total energy obtained with MSXα spin-orbitals $\tilde{u}_i$ and $F_p(\tilde{\rho}_{x\alpha})$ is the electrostatic force exerted on the nuclear coordinate X_p by the other nuclei and the electronic charge cloud $\tilde{\rho}_{x\alpha}$ formed from $\tilde{u}_i$.

(2) How well does $F_p(\tilde{\rho}_{x\alpha})$ compare with the experimental value of force acting on the nuclear coordinate X_p?

In order to answer the above questions, we made some force calculations on homonuclear diatomic molecules. The reasons that we pick the homonuclear diatomic molecules are that the α values in these systems are constant throughout the whole space which is the restriction of the Hellmann-Feynman Theorem, and that the computations are easier and the results can be compared with the experimental values.

4.4 Method of Hellmann-Feynman Force Calculations

To investigate the Hellmann-Feynman Theorem, we have to calculate two quantities, the total energy and the electrostatic force exerted by the electron cloud as expressed by the integral on the left hand side of equation (4.4). The calculation of the total energy $\overline{\langle E_{x\alpha}\rangle}$ can be done by using Danese's program (see Danese (1973)), as we have discussed in Section 2 of Chapter III. The main quantity that we want to evaluate in this discussion is the electrostatic force $F_e(\tilde{\rho}_{x\alpha})$:

$$F_e(\tilde{\rho}_{x\alpha}) = \int \tilde{\rho}_{x\alpha}(\vec{r}) \frac{\partial}{\partial X_p} \left(\frac{2Z_p}{|\vec{r}-\vec{R}_p|} \right) d^3r$$

Since $\tilde{\rho}(\vec{r}) = \sum_i n_i \tilde{u}_i^*(\vec{r})\tilde{u}_i(\vec{r})$ where n_i is the occupation number of the ith state, we can express $F_e(\tilde{\rho}_{x\alpha})$ as:

$$F_e(\tilde{\rho}_{x\alpha}) = \sum_i n_i \int \tilde{u}_i^*(\vec{r})\tilde{u}_i(\vec{r}) \frac{\partial}{\partial X_p} \left(\frac{2Z_p}{|\vec{r}-\vec{R}_p|} \right) d^3r$$

For a homonuclear diatomic molecule, the expression for the z-component, which is the only nonvanishing part, of the force exerted on nucleus A is reduced to:

$$F_e(\tilde{\rho}_{x\alpha}) = 2 Z_A \sum_i n_i \int \tilde{u}_i^*(\vec{r})\tilde{u}_i(\vec{r})\frac{\cos\Theta_A}{r_A^2} d^3r$$

To evaluate the above integrals, we partition the region of integration into four parts: one over sphere A,

one over sphere B, one over the outer sphere, and one over the intersphere region:

$$\int \tilde{u}_i^*(\vec{r})\tilde{u}_i(\vec{r}) \frac{\cos\Theta_A}{r_A^2} d^3r = F_A^i + F_B^i + F_{out}^i + F_{II}^i \qquad (4.5)$$

where $F_j^i = \int_j \tilde{u}_i^*(\vec{r})\tilde{u}_i(\vec{r}) \frac{\cos\Theta_A}{r_A^2} d^3r$, $\qquad$ j = A, B, out, II

We shall discuss each of the integrals in the following:

Integral Over Sphere A: F_A^i

Inside sphere A, we have

$$\tilde{u}_i(\vec{r}) = \sum_{\ell,m} C_{\ell m}^{iA} R_\ell(\vec{r}_A, \tilde{\varepsilon}_i) Y_\ell^m(\vec{r}_A)$$

where $C_{\ell m}^{iA}$ are the C-coefficients,

$Y_\ell^m(\vec{r}_A)$ are the real spherical harmonics centered at A.

Since we have used real functions as our basis, all the C-coefficients are real, and $\tilde{u}_i^* = \tilde{u}_i$. Therefore,

$$F_A^i = \int_A \tilde{u}_i^*(\vec{r})\tilde{u}_i(\vec{r}) \frac{\cos\Theta_A}{r_A^2} d^3r$$

$$= \sum_{\ell_1 m_1} \sum_{\ell_2 m_2} C_{\ell_1 m_1}^{iA} C_{\ell_2 m_2}^{iA} \int_A \{ R_{\ell_1}(r_A)Y_{\ell_1}^m(\vec{r}_A)$$

$$\times R_{\ell_1}(r_A)Y_{\ell_2}^m(\vec{r}_A) \frac{\cos\Theta_A}{r_A^2} \} . d^3r$$

$$= \sum_{\ell_1 m_1} \sum_{\ell_2 m_2} C_{\ell_1 m_1}^{iA} C_{\ell_2 m_2}^{iA} \int_0^{R_A} R_{\ell_1}(r_A)R_{\ell_2}(r_A)\frac{1}{r_A^2} r_A^2 dr_A$$

$$\times \int Y_{\ell_1}^{m_1}(\vec{r}_A) Y_{\ell_2}^{m_2}(\vec{r}_A) \cos\Theta_A \, d\Omega_A$$

$$= \sum_{\ell_1 m_1} \sum_{\ell_2 m_2} C_{\ell_1 m_1}^{iA} C_{\ell_2 m_2}^{iA} (4\pi/3)^{\frac{1}{2}} I(\ell_1,m_1;\ell_2,m_2;1,0)$$

$$\times \int_0^{R_A} R_{\ell_1}(r_A) R_{\ell_2}(r_A) \, dr_A$$

where $I(\ell_1,m_1;\ell_2,m_2;\ell_3,m_3)$ are the Gaunt coefficients as defined in equation (3.4).

Since $I(\ell_1,m_1;\ell_2,m_2;1,0) = 0$ unless the arguments satisfy the following conditions:

$$m_1 = m_2 = m$$
$$\ell_1 + \ell_2 + 1 \text{ is even}$$
$$|\ell_1 - \ell_2| < 1 < \ell_1 + \ell_2$$

therefore
$$F_A^i = \sum_{\substack{\ell_1, \ell_2 \\ |\ell_1 - \ell_2| \leq 1 \leq \ell_1 + \ell_2}} \sum_m C_{\ell_1 m}^{iA} C_{\ell_2 m}^{iA} (4\pi/3)^{\frac{1}{2}}$$

$$\times I(\ell_1,m;\ell_2,m;1,0) \int_0^{R_A} R_{\ell_1}(r_A) R_{\ell_2}(r_A) \, dr_A$$

By the axial symmetry of the diatomic molecule, the C-coefficients are nonzero only if $m=m_i$ for state i (henceforth called m). Therefore, we have:

$$F_A^i = \sum_{\substack{\ell_1, \ell_2 \\ |\ell_1 - \ell_2| \leq 1 \leq \ell_1 + \ell_2}} C_{\ell_1 m}^{iA} C_{\ell_2 m}^{iA} (4\pi/3)^{\frac{1}{2}}$$

$$\times I(\ell_1,m;\ell_2,m;1,0) \int_0^{R_A} R_{\ell_1}(r_A) R_{\ell_2}(r_A) \, dr_A$$

$$(4.6)$$

Integral Over Sphere B: F_B^i

Inside sphere B, we have:

$$\tilde{u}_i(\vec{r}) = \sum_{\ell} C_{\ell m}^{iB} R_{\ell}(r_B) Y_{\ell}^m(\tilde{\vec{r}}_B)$$

So
$$F_B^i = \sum_{\ell_1, \ell_2} C_{\ell_1 m}^{iB} C_{\ell_2 m}^{iB} \int_B R_{\ell_1}(r_B) Y_{\ell_1}^m(\vec{r}_B) R_{\ell_2}(r_B) Y_{\ell_2}^m(\vec{r}_B)$$

$$\times \frac{\cos\Theta_A}{r_A^2} d^3r$$

By equation (3.2), we can expand $\cos\Theta_A/r_A^2$ in terms of functions centered at B:

$$\frac{\cos\Theta_A}{r_A^2} = (4\pi/3)^{\frac{1}{2}} \frac{Y_1^0(\vec{r}_A)}{r_A^2}$$

$$= -4\pi (4\pi/3)^{\frac{1}{2}} \sum_{\ell=0}^{\infty} I(\ell+1, 0; 1, 0; \ell, 0)$$

$$\times \frac{Y_{\ell+1}^0(\vec{R}_A - \vec{R}_B)}{R_{AB}^{\ell+2}} r_B^{\ell} Y_{\ell}^0(\vec{r}_B)$$

Therefore
$$F_B^i = \sum_{\ell_1, \ell_2} C_{\ell_1 m}^{iB} C_{\ell_2 m}^{iB} (-4\pi)(4\pi/3)^{\frac{1}{2}}$$

$$\times \sum_{\ell=0}^{\infty} I(\ell+1, 0; 1, 0; \ell, 0) \frac{Y_{\ell+1}^0(\vec{R}_A - \vec{R}_B)}{R_{AB}^{\ell+2}}$$

$$\times \int_0^{R_B} R_{\ell_1}(r_B) R_{\ell_2}(r_B) r_B^{\ell+2} dr_B$$

$$\times \int Y_{\ell_1}^m(\vec{r}_B) Y_{\ell_2}^m(\vec{r}_B) Y_{\ell}^0(\vec{r}_B) d\Omega_B$$

$$F_B^i = \sum_{\ell_1, \ell_2} C_{\ell_1 m}^{iB} C_{\ell_2 m}^{iB} (-4\pi)(4\pi/3)^{\frac{1}{2}} \sum_{\substack{\ell = |\ell_1 - \ell_2| \\ \ell_1 + \ell_2 + \ell \text{ even}}}^{\ell_1 + \ell_2} \{I(\ell+1, 0; 1, 0; \ell, 0)$$

$$\times \quad I(\ell_1, m; \ell_2, m; \ell, 0) \, \frac{Y_{\ell+1}^0(\vec{R}_A - \vec{R}_B)}{R_{AB}^{\ell+2}}$$

$$\times \int_0^{R_B} R_{\ell_1}(r_B) R_{\ell_2}(r_B) r_B^{\ell+2} dr_B\} \tag{4.7}$$

Integral Over the Outer Sphere: F_{out}^i

Inside the outer sphere, we have:

$$\tilde{u}_i(\vec{r}) = \sum_{\ell} C_{\ell m}^{i0} \, R_\ell(r_0) \, Y_\ell^m(\vec{r}_0)$$

Thus $\quad F_{out}^i = \sum_{\ell_1, \ell_2} C_{\ell_1 m}^{i0} C_{\ell_2 m}^{i0} \int_{out} \{R_{\ell_1}(r_0) Y_{\ell_1}^m(\vec{r}_0) R_{\ell_2}(r_0) Y_{\ell_2}^m(\vec{r}_0)$

$$\times \frac{\cos\Theta_A}{r_A^2}\} d^3 r$$

By equation (3.3), we expand $\cos\Theta_A / r_A^2$ around the center of the outer sphere 0. After integrating over Ω_A, we have:

$$F_{out}^i = 4\pi(4\pi/3)^{\frac{1}{2}} \sum_{\ell_1, \ell_2} C_{\ell_1 m}^{i0} C_{\ell_2 m}^{i0} \sum_{\substack{\ell' = |\ell_1 - \ell_2| \\ \ell' \geq 1, \ \ell' + \ell_1 + \ell_2 \text{ even}}}^{\ell_1 + \ell_2} \{I(\ell'-1, 0; 1, 0; \ell', 0)$$

$$\times \quad I(\ell_1, m; \ell_2, m; \ell', 0) \, R_{A0}^{\ell'-1} Y_{\ell'-1}^0(\vec{R}_A - \vec{R}_0)$$

$$\times \int_{R_0}^{\infty} \frac{R_{\ell_1}(r_0) R_{\ell_2}(r_0)}{r_0^{\ell'-1}} \, dr_0 \} \tag{4.8}$$

Integral Over the Intersphere Region: F_{II}^i

In the intersphere region, $\tilde{u}_i$ can be expressed as:

$$\tilde{u}_i(\vec{r}) = \begin{cases} \displaystyle\sum_{\ell_1} A_{\ell_1 m}^{iA} \eta_{\ell_1}(\kappa r_A) Y_{\ell_1}^m(\vec{r}_A) + \sum_{\ell_2} A_{\ell_2 m}^{iB} \eta_{\ell_2}(\kappa r_B) Y_{\ell_2}^m(\vec{r}_B) \\ \\ + \displaystyle\sum_{\ell_3} A_{\ell_3 m}^{i0} j_{\ell_3}(\kappa r_0) Y_{\ell_3}^m(\vec{r}_0) \qquad \text{if } \overset{\sim}{\epsilon}_i > \overline{V}_{II} \\ \\ \displaystyle\sum_{\ell_1} A_{\ell_1 m}^{iA} k_{\ell_1}(\kappa r_A) Y_{\ell_1}^m(\vec{r}_A) + \sum_{\ell_2} A_{\ell_2 m}^{iB} k_{\ell_2}(\kappa r_B) Y_{\ell_2}^m(\vec{r}_B) \\ \\ + \displaystyle\sum_{\ell_3} A_{\ell_3 m}^{i0} i_{\ell_3}(\kappa r_0) Y_{\ell_3}^m(\vec{r}_0) \qquad \text{if } \overset{\sim}{\epsilon}_i < \overline{V}_{II} \end{cases}$$

For diatomic molecules, the eigenvalues $\overset{\sim}{\epsilon}_i$ for most states (except the core state) are greater than the constant potential $\overline{V}_{II}$ in the intersphere region. We shall look at the positive energy case ($\overset{\sim}{\epsilon}_i > \overline{V}_{II}$) in more detail (the other case can be treated in a similar way). For core states, the electronic charge is concentrated around the atomic centers and the contribution due to the intersphere region can be neglected in the core states. Thus, we have the following expression for F_{II}^i:

$$F_{II}^i = \int_{II} \tilde{u}_i^*(\vec{r}) \tilde{u}_i(\vec{r}) \frac{\cos\theta_A}{r_A^2} d^3r$$

$$= \sum_{\ell_1, \ell_2} A_{\ell_1 m}^{iA} A_{\ell_2 m}^{iA} I_{AA}^i(\ell_1, \ell_2, m) + \sum_{\ell_1, \ell_2} A_{\ell_1 m}^{iB} A_{\ell_2 m}^{iB} I_{BB}^i(\ell_1, \ell_2, m)$$

$$+ \sum_{\ell_1, \ell_2} A_{\ell_1 m}^{i0} A_{\ell_2 m}^{i0} I_{00}^i(\ell_1, \ell_2, m) + 2\sum_{\ell_1, \ell_2} A_{\ell_1 m}^{iA} A_{\ell_2 m}^{iB} I_{AB}^i(\ell_1, \ell_2, m)$$

$$+ 2 \sum_{\ell_1, \ell_2} A^{iA}_{\ell_1 m} A^{i0}_{\ell_2 m} I^i_{A0}(\ell_1, \ell_2, m) + 2 \sum_{\ell_1, \ell_2} A^{iB}_{\ell_1 m} A^{i0}_{\ell_2 m} I^i_{B0}(\ell_1, \ell_2, m)$$

$$(4.9)$$

where

$$I^i_{AA}(\ell_1, \ell_2, m) = \int_{II} \eta_{\ell_1}(\kappa r_A) Y^m_{\ell_1}(\vec{r}_A) \eta_{\ell_2}(\kappa r_A) Y^m_{\ell_2}(\vec{r}_A)$$

$$\times \frac{\cos\theta_A}{r_A^2} d^3r$$

$$I^i_{BB}(\ell_1, \ell_2, m) = \int_{II} \eta_{\ell_1}(\kappa r_B) Y^m_{\ell_1}(\vec{r}_B) \eta_{\ell_2}(\kappa r_B) Y^m_{\ell_2}(\vec{r}_B)$$

$$\times \frac{\cos\theta_A}{r_A^2} d^3r$$

$$I^i_{AB}(\ell_1, \ell_2, m) = \int_{II} \eta_{\ell_1}(\kappa r_A) Y^m_{\ell_1}(\vec{r}_A) \eta_{\ell_2}(\kappa r_B) Y^m_{\ell_2}(\vec{r}_B)$$

$$\times \frac{\cos\theta_A}{r_A^2} d^3r$$

$$I^i_{A0}(\ell_1, \ell_2, m) = \int_{II} \eta_{\ell_1}(\kappa r_A) Y^m_{\ell_1}(\vec{r}_A) j_{\ell_2}(\kappa r_0) Y^m_{\ell_2}(\vec{r}_0)$$

$$\times \frac{\cos\theta_A}{r_A^2} d^3r$$

$$I^i_{B0}(\ell_1, \ell_2, m) = \int_{II} \eta_{\ell_1}(\kappa r_B) Y^m_{\ell_1}(\vec{r}_B) j_{\ell_2}(\kappa r_0) Y^m_{\ell_2}(\vec{r}_0)$$

$$\times \frac{\cos\theta_A}{r_A^2} d^3r$$

$$I^i_{00}(\ell_1, \ell_2, m) = \int_{II} j_{\ell_1}(\kappa r_0) Y^m_{\ell_1}(\vec{r}_0) j_{\ell_2}(\kappa r_0) Y^m_{\ell_2}(\vec{r}_0)$$

$$\times \frac{\cos\theta_A}{r_A^2} d^3r$$

To evaluate each of the above integrals, we employ Prolate Spheroidal Coordinates as introduced in Section 2 at the beginning of this chapter. First of all, we want to see what the limits of integration are for such coordinates.

For the intersphere region, we have the following restrictions on ξ and η:

(1) $r_A + r_B \geqslant R$ or $\xi = (r_A + r_B)/R \geqslant 1$

(2) $| r_A - r_B | \leqslant R$ or $| \eta | = |(r_A - r_B)/R| \leqslant 1$

(3) $r_A \geqslant R_A = R/2$ or $\xi + \eta \geqslant 1$

(4) $r_B \geqslant R_B = R/2$ $\xi - \eta \geqslant 1$

(5) From figure (4.2), we have:

$$r_0^2 = r_A^2 + (R/2)^2 - 2r_A(R/2)\cos\theta_A$$

$$= (R/2)^2(\xi+\eta)^2 + (R/2)^2 - 2(R/2)(\xi+\eta)(R/2)(1+\xi\eta)/(\xi+\eta)$$

$$= (R/2)^2 (\xi^2 + \eta^2 - 1)$$

Since $r_0 \leqslant R$, we have $\xi^2 + \eta^2 \leqslant 5$

Putting all of the restrictions together, we have
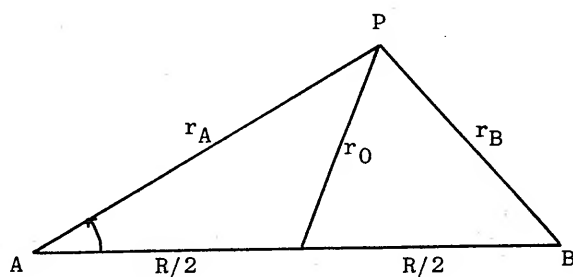
Fig. 4.2   Relation of r_A, R and θ_A
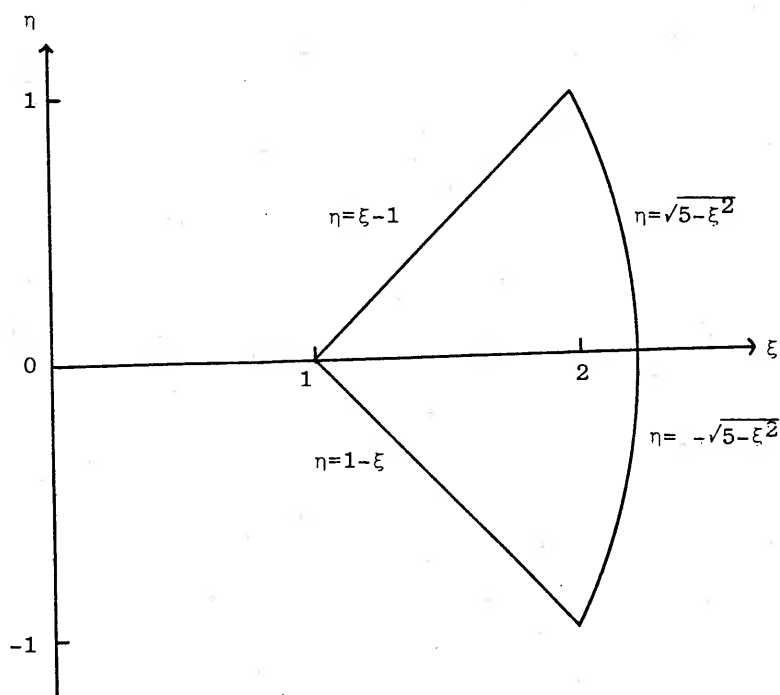
Fig. 4.3   Boundary of the Intersphere Region in
Prolate Spheroidal Coordinates with A
and B as the Foci.

the transformed intersphere region as defined by: (figure 4.3)

$$-f(\xi) \leqslant \xi \leqslant f(\xi) \qquad \text{and} \qquad 1 \leqslant \xi \leqslant \sqrt{5}$$

where

$$f(\xi) = \begin{cases} \xi - 1 & \text{if } 1 \leqslant \xi \leqslant 2 \\ \\ (5 - \xi)^{\frac{1}{2}} & \text{if } 2 \leqslant \xi \leqslant \sqrt{5} \end{cases}$$

Before discussing the evaluation of the integrals, we note that all the integrands, except for the factor of the spherical harmonics, are ϕ-independent, and, because of the cylindrical symmetry of the intersphere region, all the integrals can be reduced into two-dimensional integrals through the ϕ-integration, such as:

$$\int_{II} \eta_{\ell_1}(\kappa r_A) Y_{\ell_1}^m(\vec{r}_A) \eta_{\ell_2}(\kappa r_B) Y_{\ell_2}^m(\vec{r}_B) \cos\Theta_A / r_A^2 \, d^3r$$

$$= \int_{II} \eta_{\ell_1}(\kappa r_A) P_{\ell_1}^m(\cos\Theta_A) \eta_{\ell_2}(\kappa r_B) P_{\ell_2}^m(\cos\Theta_B) \cos\Theta_A / r_A^2 d^3r / d\phi$$

where P_ℓ^m are the normalized Legendre polynomials.

To evaluate the integrals, we also introduce the following expressions for P_ℓ^m, η_ℓ and j_ℓ:

$$P_\ell^m(\cos\Theta_A) = N_\ell^m(\sin\Theta_A)^m \sum_{\nu = 0}^{[\frac{1}{2}(\ell-m)]} \omega_\nu^{\ell m}(\cos\Theta_A)^{\ell-m-2\nu}$$

$$\eta_\ell(z) = (-1)^{\ell+1} z^{-1} \{Q^0(\ell+\tfrac{1}{2},z)\cos(z+\tfrac{1}{2}\ell\pi) - Q^1(\ell+\tfrac{1}{2},z)\sin(z+\tfrac{1}{2}\ell\pi)\}$$

$$j_\ell(z) = z^{-1} \{Q^0(\ell+\tfrac{1}{2},z)\sin(z-\tfrac{1}{2}\ell\pi) + Q^1(\ell+\tfrac{1}{2},z)\cos(z-\tfrac{1}{2}\ell\pi)\}$$

where $\quad N_\ell^m = (-1)^m \{\dfrac{(2\ell+1)(\ell-m)!}{2\ (\ell+m)!}\}^{\frac{1}{2}}$

$$\omega_\nu^{\ell m} = (-1)^\nu \frac{(2\ell-2\nu)!}{2^\ell(\ell-m-2\nu)!(\ell-\nu)!\nu!}$$

$$Q^0(\ell+\tfrac{1}{2},z) = \sum_{k=0}^{[\ell/2]} (-1)^k (\ell+\tfrac{1}{2},2k)(2z)^{-2k} \qquad (4.10)$$

$$Q^1(\ell+\tfrac{1}{2},z) = \sum_{k=0}^{[(\ell-1)/2]} (-1)^k (\ell+\tfrac{1}{2},2k+1)(2z)^{-2k-1}$$

$$(\ell+\tfrac{1}{2},k) = \frac{(\ell+k)!}{k!(\ell-k)!}$$

and $\quad [b]$ = the integer part of the real number b.

With the above expressions and some algebra, we have the following results for I_{AA}^i, I_{BB}^i, I_{AB}^i, I_{AO}^i, I_{BO}^i, and I_{OO}^i as required by equation (4.9):

(1) $I_{AA}^i:$ $\displaystyle\int_{11} \eta_{\ell_1}(\kappa r_A) Y_{\ell_1}^m(\vec{r}_A) \eta_{\ell_2}(\kappa r_A) Y_{\ell_2}^m(\vec{r}_A)\cos\theta_A/r_A^2\, d^3r$

This is a one-center integral. With some straight-forward algebra, we have:

$$I^i_{AA} = N^m_{\ell_1} N^m_{\ell_2} (-1)^{\ell_1+\ell_2} (R/2) \int_1^{\sqrt{5}} d\xi \{ \sum_{\nu_1=0}^{[(\ell_1-m)/2]} \sum_{\nu_2=0}^{[(\ell_2-m)/2]} \sum_{n=0}^{m} \sum_{s=0}^{\ell_1+\ell_2-2m+1-2\nu+2r}$$

$$\{ \omega^{\ell_1 m}_{\nu_1} \omega^{\ell_2 m}_{\nu_2} (-1)^r C^m_r (\kappa R)^{\ell_1+\ell_2-2m+1-2\nu+2r} C^{\ell_1+\ell_2-2m+1-2\nu+2r}_r$$

$$\times (\kappa R)^{-s} \xi^s (1-\xi^2)^{\ell_1+\ell_2-2m+1-2\nu+2r-s}$$

$$\times \{ 4\xi g^1_{\ell_1\ell_2} (\ell_1+\ell_2-2m-2\nu+2r-s+4, \xi)$$

$$- (2/\kappa R) g^1_{\ell_1\ell_2} (\ell_1+\ell_2-2m-2\nu+2r-s+3, \xi) \} \} \qquad (4.11)$$

where $\nu = \nu_1 + \nu_2$

$$C^m_r = \frac{m!}{(m-r)! \, r!}$$

Here the g^1 -functions are defined as:

$$g^1_{\ell_1\ell_2} (\ell_3, \xi) = \sum_{u=0}^{1} \sum_{v=0}^{1} \sum_{n=0}^{[\frac{1}{2}(\ell_1-u)]+[\frac{1}{2}(\ell_2-v)]} (-1)^{u+v}$$

$$\times A^{(u,v)}_n P^{(u,v,1)}_{\ell_1\ell_2} (\ell_3+2n+u+v, \xi)$$

where the A-coefficients are defined in terms of the $(\ell+\frac{1}{2}, k)$ coefficients through the following relations:

$$\sum_{n=0}^{[\frac{1}{2}(\ell_1-u)]+[\frac{1}{2}(\ell_2-v)]} A^{(u,v)}_n (2z)^{-n} = Q^u (\ell_1+\frac{1}{2}, z) Q^v (\ell_2+\frac{1}{2}, z)$$

and $P_{\ell_1 \ell_2}^{(u,v,1)}(\ell,\xi)$ are defined in terms of the sine and cosine integrals as below:

$$P_{\ell_1 \ell_2}^{(u,v,1)}(\ell,\xi) = \{\cos\tfrac{1}{2}(\ell_1+\ell_2)\pi \ (\delta_{u+v,0} - \delta_{u+v,2})$$

$$+ \sin\tfrac{1}{2}(\ell_1+\ell_2)\pi \ \delta_{u+v,1}\} \int_{\kappa R(\xi-f(\xi))}^{\kappa R(\xi+f(\xi))} \frac{\cos t}{t^\ell} \, dt$$

$$+ \{\sin\tfrac{1}{2}(\ell_1+\ell_2)\pi \ (\delta_{u+v,2} - \delta_{u+v,0})$$

$$+ \cos\tfrac{1}{2}(\ell_1+\ell_2)\pi \ \delta_{u+v,1}\} \int_{\kappa R(\xi-f(\xi))}^{\kappa R(\xi+f(\xi))} \frac{\sin t}{t^\ell} \, dt$$

$$+ \{\cos\tfrac{1}{2}(\ell_1-\ell_2)\pi \ (\delta_{u+v,0} + \delta_{u+v,2})$$

$$+ \sin\tfrac{1}{2}(\ell_1-\ell_2)\pi \ \delta_{u+v,1}(\delta_{v0}-\delta_{v1})\} \int_{\kappa R(\xi-f(\xi))}^{\kappa R(\xi+f(\xi))} \frac{dt}{t^\ell}$$

(2) I_{BB}^i: $\displaystyle\int_{II} \eta_{\ell_1}(\kappa r_B) Y_{\ell_1}^m(\vec{r}_B) \eta_{\ell_2}(\kappa r_B) Y_{\ell_2}^m(\vec{r}_B) \cos\Theta_A / r_A^2 \, d^3r$

This is a two-center integral. The result is as following:

$$I_{BB}^i = N_{\ell_1}^m N_{\ell_2}^m \ (-1)^{\ell_1+\ell_2+1}(R/2) \int_1^{\sqrt{5}} d\xi \{ \sum_{\nu_1=0} \sum_{\nu_2=0} \sum_{\lambda=0}^{[\frac{1}{2}(\ell_1-m)]} \sum_{s=0}^{[\frac{1}{2}(\ell_2-m)]} \sum^m \sum^{\ell_1+\ell_2-2m-2\nu+2r}$$

$$\times \{\omega_{\nu_1}^{\ell_1 m} \omega_{\nu_2}^{\ell_2 m} C_r^m (-1)^{\ell_1+\ell_2-2m-2\nu+3r} C_s^{\ell_1+\ell_2-2m-2\nu+2r}$$

$$\times (\kappa R)^s 2(1-\xi^2)^s \xi^{\ell_1+\ell_2-2m-2\nu+2r-s} \{(1+\xi^2) g_{\ell_1\ell_2}^2(s+1,\xi)$$

$$- (\xi/\kappa R) g_{\ell_1\ell_2}^2(s,\xi)\}\} \tag{4.12}$$

where $\nu = \nu_1 + \nu_2$

and the g^2-functions are defined as:

$$g^2_{\ell_1\ell_2}(s,\xi) = \sum_{u=0}^{\ell} \sum_{v=0}^{\ell} \sum_{n=0}^{[\frac{1}{2}(\ell_1-u)]+[\frac{1}{2}(\ell_2-v)]} (-1)^{u+v}$$

$$\times A_n^{(u,v)} \, P_{\ell_1\ell_2}^{(u,v,2)}(s+2n+u+v+1,\xi)$$

where the A-coefficients are defined as in I_{AA}^i, and $P_{\ell_1\ell_2}^{(u,v,2)}(\ell,\xi)$ are defined in terms of the sine and cosine integrals as below:

$$P_{\ell_1\ell_2}^{(u,v,2)}(\ell,\xi) = \{\cos\tfrac{1}{2}(\ell_1+\ell_2)\pi \; (\delta_{u+v,0} - \delta_{u+v,2})$$

$$+ \sin\tfrac{1}{2}(\ell_1+\ell_2)\pi\delta_{u+v,1}\} \int_{\kappa R(\frac{1}{2}-f(\frac{1}{2}))}^{\kappa R(\frac{1}{2}+f(\frac{1}{2}))} \frac{\cos t}{(2\kappa R\xi-t)^2 t^\ell} \, dt$$

$$+\{\sin\tfrac{1}{2}(\ell_1+\ell_2)\pi \; (\delta_{u+v,2} - \delta_{u+v,0})$$

$$+ \cos\tfrac{1}{2}(\ell_1+\ell_2)\pi\delta_{u+v,1}\} \int_{\kappa R(\frac{1}{2}-f(\frac{1}{2}))}^{\kappa R(\frac{1}{2}+f(\frac{1}{2}))} \frac{\sin t}{(2\kappa R\xi-t)^2 t^\ell} \, dt$$

$$+\{\cos\tfrac{1}{2}(\ell_1-\ell_2)\pi \; (\delta_{u+v,0} - \delta_{u+v,2})$$

$$+ \sin\tfrac{1}{2}(\ell_1-\ell_2)\pi \; (\delta_{v0} - \delta_{v1})\delta_{u+v,1}\}$$

$$\times \int_{\kappa R(\frac{1}{2}-f(\frac{1}{2}))}^{\kappa R(\frac{1}{2}+f(\frac{1}{2}))} \frac{1}{(2\kappa R\xi-t)^2 t^\ell} \, dt$$

(3) I_{AB}^i: $\displaystyle\int_{II} \eta_{\ell_1}(\kappa r_A) Y_{\ell_1}^m(\vec{r}_A) \eta_{\ell_2}(\kappa r_A) Y_{\ell_2}^m(\vec{r}_A) \cos\theta_A / r_A^2 \, d^3r$

This is also a two-center integral. The result is:

$$I_{AB}^i = N_{\ell_1}^m \, N_{\ell_2}^m \, (-1)^{\ell_1+\ell_2}(R/2) \int_1^{\sqrt{5}} d\xi \; \left\{ \sum_{u=0}^{m} \sum_{v=0}^{2u} \sum_{\nu_1=0}^{[\frac{1}{2}(\ell_1-m)]} \sum_{r=0}^{\ell_1-m-2\nu_1} \right.$$

$$\sum_{\nu_2=0}^{[\frac{1}{2}(\ell_2-m)]} \sum_{s=0}^{\ell_2-m-2\nu_2} \times (-1)^{u+v+\ell_2-2\nu_2} \; C_u^m \; C_v^{2u} \; C_r^{\ell_1-m-2\nu_1} \; \omega_{\nu_1}^{\ell_1 m} \; \omega_{\nu_2}^{\ell_2 m}$$

$$\times C_s^{\ell_2-m-2\nu_2} \; (\kappa R)^{\ell_1+\ell_2-2\nu_1-2\nu_2-2u+v-s-r} \; \xi^{v+r+s}$$

$$\times\{2(1-\xi^2) \; g_{\ell_1\ell_2}^3(\ell_1-2\nu_1-2u+v-r+3, \ell_2-2\nu_2-s, \xi)$$

$$\frac{2\xi}{\kappa R} \; g_{\ell_1\ell_2}^3(\ell_1-2\nu_1-2u+v-r+2, \ell_2-2\nu_2-s, \xi)\}\}\} \quad (4.13)$$

where the g^3-functions are defined as:

$$g_{\ell_1\ell_2}^3(\ell_1,\ell_2,\xi) = \sum_{u=0}^{1} \sum_{v=0}^{1} \sum_{k_1=0}^{[\frac{1}{2}(\ell_1-u)]} \sum_{k_2=0}^{[\frac{1}{2}(\ell_2-v)]} (-1)^{u+v+k_1+k_2} \; (\ell_1+\tfrac{1}{2}, 2k_1+u)$$

$$\times (\ell_2+\tfrac{1}{2}, 2k_2+v) \; P_{\ell_1\ell_2}^{(u,v,3)}(\ell_3+2k_1+u, \ell_4+2k_2+v, \xi)$$

and $P_{\ell_1\ell_2}^{(u,v,3)}(r,s,\xi)$ are defined in terms of the sine and cosine integrals as below:

$$P_{\ell_1\ell_2}^{(u,v,3)}(r,s,\xi)$$

$$= \{\cos(\kappa R\xi + \frac{\ell_1-\ell_2}{2}\pi)(\delta_{u+v,0} + \delta_{u+v,2})$$

$$+ \sin(\kappa R\xi+\frac{\ell_1-\ell_2}{2}\pi)\delta_{u+v,1}(\delta_{v0}-\delta_{v1})\} \int_{\kappa R(\xi-f(\xi))}^{\kappa R(\xi+f(\xi))} \frac{\cos t}{(2\kappa R\xi-t)^r t^s} dt$$

$$+\{\sin(\kappa R\xi+\frac{\ell_1-\ell_2}{2}\pi)(\delta_{u+v,0}+\delta_{u+v,2})$$

$$+ \cos(\kappa R\xi+\frac{\ell_1-\ell_2}{2}\pi)\delta_{u+v,1}(\delta_{u0}-\delta_{u1})\} \int_{\kappa R(\xi-f(\xi))}^{\kappa R(\xi+f(\xi))} \frac{\sin t}{(2\kappa R\xi-t)^r t^s}dt$$

$$+\{\cos(\kappa R\xi+\frac{\ell_1+\ell_2}{2}\pi)(\delta_{u+v,0}-\delta_{u+v,2})$$

$$+ \sin(\kappa R\xi+\frac{\ell_1+\ell_2}{2}\pi)\delta_{u+v,1}\} \int_{\kappa R(\xi-f(\xi))}^{\kappa R(\xi+f(\xi))} \frac{1}{(2\kappa R\xi-t)^r t^s} dt$$

(4) I_{A0}^i: $\int_{II} \eta_{\ell_1}(\kappa r_A)Y_{\ell_1}^m(\vec{r}_A)j_{\ell_2}(\kappa r_0)Y_{\ell_2}^m(\vec{r}_0)\cos\Theta_A/r_A^2 \, d^3r$

Here we have a two-center integral. We want to express $j_{\ell_2}(\kappa r_0)Y_{\ell_2}^m(\vec{r}_0)$ in terms of functions centered at A so that we can reduce the integral into sums of one-center integrals. Such an expansion is derived in Appendix E:

$$j_{\ell_2}(\kappa r_0)Y_{\ell_2}^m(\vec{r}_0) = (-1)^{\ell_2}4\pi \sum_{\ell',m'} \sum_{\ell'',m''} i^{\ell'-\ell_2-\ell''}$$

$$\times I(\ell'',m'';\ell_2,m;\ell',m') (-1)^{\ell'}$$

$$\times j_{\ell'}(\kappa R_A)Y_{\ell'}^m(\vec{R}_A)j_{\ell''}(\kappa r_A)Y_{\ell''}^m(\vec{r}_A) \qquad (4.14)$$

for $\vec{r}_0$ in the intersphere region.

With the above equation, we have:

$$I_{AO}^i = (-1)^{\ell_2} 4\pi \sum_{\ell'=0}^{\infty} \sum_{\substack{\ell''=|\ell_2-\ell'| \\ \ell''+\ell_2+\ell'=2k}}^{\ell_2+\ell'} (-1)^k \, I(\ell'',m;\ell_2,m;\ell',0)$$

$$\times \, j_{\ell'}(\kappa R_A) Y_{\ell'}^0(\vec{R}_A) \int_{II} j_{\ell_2}(\kappa r_A) Y_{\ell_2}^m(\vec{r}_A) j_{\ell''}(\kappa r_A) Y_{\ell''}^m(\vec{r}_A)$$

$$\times \, \frac{\cos\Theta_A}{r_A^2} \, d^3r \qquad\qquad (4.15)$$

Thus, we reduce I_{AO}^i to an infinite sum of one-center integrals. Since $j_{\ell'}$ decreases rapidly with increasing ℓ', we can expect that the sum would converge rapidly.

To evaluate the integral on the RHS of equation (4.15), we employ the same technique as before and obtain the following expression:

$$\int_{II} \eta_{\ell_1}(\kappa r_A) Y_{\ell_1}^m(\vec{r}_A) j_{\ell_2}(\kappa r_A) Y_{\ell_2}^m(\vec{r}_A) \cos\Theta_A / r_A^2 \, d^3r$$

$$= N_{\ell_1}^m N_{\ell_2}^m (-1)^{\ell_1+1} (R/2) \int_1^{\sqrt{5}} d\xi \{ \sum_{\nu_1=0}^{[\frac{1}{2}(\ell_1-m)]} \sum_{\nu_2=0}^{[\frac{1}{2}(\ell_2-m)]} \sum_{r=0}^{m} \sum_{s=0}^{\ell_1+\ell_2-2m-2\nu+2r+1}$$

$$\times(-1)^r \omega_{\nu_1}^{\ell_1 m} \omega_{\nu_2}^{\ell_2 m} C_r^m C_s^{\ell_1+\ell_2-2m-2\nu+2r+1} (\kappa R)^s (1-\xi^2)^s$$

$$\times \xi^{\ell_1+\ell_2-2m+1-2\nu+2r-s} \{ 4\xi \, g_{\ell_1\ell_2}^4(s+3,\xi) - \frac{2}{\kappa R} g_{\ell_1\ell_2}^4(s+2,\xi) \} \}$$

$$\qquad\qquad (4.16)$$

where $\nu = \nu_1 + \nu_2$

and the g^4-functions are defined as:

$$g_{\ell_1\ell_2}^4(\ell_3,\xi) = \sum_{u=0}^{1} \sum_{v=0}^{1} \sum_{n=0}^{[\frac{1}{2}(\ell_1-u)]+[\frac{1}{2}(\ell_2-v)]} (-1)^u A_n^{(u,v)} P_{\ell_1\ell_2}^{(u,v,4)}(\ell_3+2n+u+v,\xi)$$

where $P_{\ell_1\ell_2}^{(u,v,4)}(\ell,\xi)$ are defined in terms of the sine and cosine integrals as below:

$$P_{\ell_1\ell_2}^{(u,v,4)}(\ell,\xi) = \{\sin\tfrac{1}{2}(\ell_1-\ell_2)\pi\ (\delta_{u+v,0}+\delta_{u+v,2})$$

$$+ \cos\tfrac{1}{2}(\ell_1-\ell_2)\pi\ \delta_{u+v,1}(\delta_{u0}-\delta_{u1})\}\int_{\kappa R(\xi-f(\xi))}^{\kappa R(\xi+f(\xi))}\frac{\cos t}{t^\ell}dt$$

$$+\{\cos\tfrac{1}{2}(\ell_1-\ell_2)\pi\ (\delta_{u+v,0}+\delta_{u+v,0})$$

$$+ \sin\tfrac{1}{2}(\ell_1-\ell_2)\pi\ \delta_{u+v,1}(\delta_{u1}-\delta_{u0})\}\int_{\kappa R(\xi-f(\xi))}^{\kappa R(\xi+f(\xi))}\frac{\sin t}{t^\ell}dt$$

$$+\{\sin\tfrac{1}{2}(\ell_1+\ell_2)\pi\ (\delta_{u+v,2}-\delta_{u+v,0})$$

$$+ \cos\tfrac{1}{2}(\ell_1+\ell_2)\pi\ \delta_{u+v,1}\}\int_{\kappa R(\xi-f(\xi))}^{\kappa R(\xi+f(\xi))}\frac{dt}{t^\ell}$$

(5) I_{B0}^i: $\displaystyle\int_{II} \eta_{\ell_1}(\kappa r_B)Y_{\ell_1}^m(\vec{r}_B)j_{\ell_2}(\kappa r_0)Y_{\ell_2}^m(\vec{r}_0)\cos\Theta_A/r_A^2\ d^3r$

Expanding $j_{\ell_2}(\kappa r_0)Y_{\ell_2}^m(\vec{r}_0)$ in terms of functions centered at at B, we have, similar to I_{A0}, the following equation:

$$I_{B0}^i = (-1)^{\ell_2}4\pi\sum_{\ell'=0}^{\infty}\sum_{\substack{\ell''=|\ell_2-\ell'|\\ \ell''+\ell_2+\ell'=2k}}^{\ell_2+\ell'}(-1)^k\ I(\ell'',m;\ell_2,m;\ell',0)$$

$$\times\ j_{\ell'}(\kappa R_B)Y_{\ell'}^m(\vec{R}_B)\int_{II}\eta_{\ell_1}(\kappa r_B)Y_{\ell_1}^m(\vec{r}_B)j_{\ell''}(\kappa r_B)Y_{\ell''}^m(\vec{r}_B)$$

$$\times\ \cos\Theta_A/r_A^2\ d^3r$$

The integral on the RHS of the above equation can be evaluated as below:

$$\int_{II} \eta_{\ell_1}(\kappa r_B) Y_{\ell_1}(\vec{r}_B) j_{\ell''}(\kappa r_B) Y_{\ell''}(\vec{r}_B) \cos\Theta_A / r_A^2 \, d^3r$$

$$= N_{\ell_1}^m N_{\ell_2}^m (-1)^{\ell_1+1} (R/2) \int_1^{\sqrt{5}} d\xi \sum_{\gamma_1=0}^{[\frac{1}{2}(\ell_1-m)]} \sum_{\gamma_2=0}^{[\frac{1}{2}(\ell_2-m)]} \sum_{r=0}^{m} \sum_{s=0}^{\ell_1+\ell_2-2m-2\nu+2r}$$

$$\times (-1)^{\ell_1+\ell_2-2m-2\nu+3r} \, \omega_{\nu_1}^{\ell_1 m} \, \omega_{\nu_2}^{\ell_2 m} \, C_r^m \, C_s^{\ell_1+\ell_2-2m-2\nu+2r} \, 2(\kappa R)^s$$

$$\times (1-\xi^2)^s \, \xi^{\ell_1+\ell_2-2m-2\nu+2r-s} \{(1+\xi^2)g_{\ell_1\ell_2}^5(s+1,\xi) - \frac{\xi}{\kappa R}g_{\ell_1\ell_2}^5(s,\xi)\}$$

where $\nu = \nu_1 + \nu_2$

and the g^5-functions are defined as:

$$g_{\ell_1\ell_2}^5(s,\xi) = \sum_{u=0}^{1} \sum_{v=0}^{1} \sum_{n=0}^{[\frac{1}{2}(\ell_1-u)]+[\frac{1}{2}(\ell_2-v)]} (-1)^u A_n(u,v) P_{\ell_1\ell_2}^{(u,v,5)}(s+2n+u+v+1,\xi)$$

where the $P_{\ell_1\ell_2}^{(u,v,5)}(\ell,\xi)$ are defined in terms of sine and cosine integrals as:

$$P_{\ell_1\ell_2}^{(u,v,5)}(\ell,\xi) = \{\sin\frac{1}{2}(\ell_1-\ell_2)\pi \ (\delta_{u+v,0} + \delta_{u+v,2})$$

$$+ \cos\frac{1}{2}(\ell_1-\ell_2)\pi \ \delta_{u+v,1}(\delta_{u0}-\delta_{u1})\}$$

$$\times \int_{\kappa R(\frac{3}{2}-f(\frac{3}{2}))}^{\kappa R(\frac{3}{2}+f(\frac{3}{2}))} \frac{\cos t}{(2\kappa R\xi-t)^2 t} \, dt$$

$$+\{\cos\frac{1}{2}(\ell_1-\ell_2)\pi \ (\delta_{u+v,0} + \delta_{u+v,2})$$

$$+ \sin\tfrac{1}{2}(\ell_1 - \ell_2)\pi \; \delta_{u+v,1}(\delta_{u1} - \delta_{u0})\}$$

$$\times \int_{\kappa R(\frac{1}{3} - f(\frac{1}{3}))}^{\kappa R(\frac{1}{3} + f(\frac{1}{3}))} \frac{\sin t}{(2\kappa R\xi - t)^2 t^\ell} \; dt$$

$$+ \{\sin\tfrac{1}{2}(\ell_1 + \ell_2)\pi \; (\delta_{u+v,2} - \delta_{u+v,0})$$

$$+ \cos\tfrac{1}{2}(\ell_1 + \ell_2)\pi \; \delta_{u+v,1}\} \times \int_{\kappa R(\frac{1}{3} - f(\frac{1}{3}))}^{\kappa R(\frac{1}{3} + f(\frac{1}{3}))} \frac{1}{(2\kappa R\xi - t)^2 t^\ell} \; dt$$

(6) I_{00}^i: $\displaystyle\int_{II} j_{\ell_1}(\kappa r_0) Y_{\ell_1}^m(\vec{r}_0) j_{\ell_2}(\kappa r_0) Y_{\ell_2}^m(\vec{r}_0) \cos\Theta_A / r_A^2 \; d^3r$

Expanding $j_\ell(\kappa r_0) Y_\ell^m(\vec{r}_0)$ about A, we have:

$$I_{00}^i = \sum_{r=0}^{\infty} \sum_{s=0}^{r} j_s(\kappa R_A) Y_s^0(\vec{R}_A) j_{r-s}(\kappa R_A) Y_{r-s}^0(\vec{R}_A) C_{s,r-s}^{\ell_1, \ell_2, m}$$

where $C_{\ell', \ell_3}^{\ell_1, \ell_2, m} = (-1)^{\ell_1 + \ell_2} (4\pi)^2 \displaystyle\sum_{\substack{\ell'' = |\ell' - \ell_1| \\ \ell'' + \ell_1 + \ell' = 2P_1}}^{\ell' + \ell_1} \sum_{\substack{\ell_4 = |\ell_3 - \ell_2| \\ \ell_4 + \ell_3 + \ell_2 = 2P_2}}^{\ell_3 + \ell_2}$

$$\{ (-1)^{p_1 + p_2} I(\ell'', m; \ell_1, m; \ell', 0)$$

$$\times I(\ell_4, m; \ell_2, m; \ell_3, 0) \; I_{\ell'', \ell_4}^{(m)} \}$$

and $I_{\ell'', \ell_4}^{(m)} = \displaystyle\int_{II} j_{\ell''}(\kappa r_A) Y_{\ell''}^m(\vec{r}_A) j_{\ell_4}(\kappa r_A) Y_{\ell_4}^m(\vec{r}_A) \cos\Theta_A / r_A^2 \; d^3r$

$$= \sum_{\ell_3 = |\ell'' - \ell_4|}^{\ell'' + \ell_4} I(\ell'', m; \ell_4, m; \ell_3, 0) \int_{II} j_{\ell''}(\kappa r_A) j_{\ell_4}(\kappa r_A)$$

$$\times Y_{\ell_3}^0(\vec{r}_A) \cos\Theta_A / r_A^2 \; d^3r$$

Thus, I_{00} is reduced to a sum of one-center integrals which, by employing the Prolate Spheroidal Coordinates, can be further reduced as below:

$$\int_{II} j_{\ell_1}(\kappa r_A) j_{\ell_2}(\kappa r_A) Y_{\ell_3}^0(\vec{r}_A)\cos\Theta_A / r_A^2 \, d^3r$$

$$= (2\ell_3+1)^{\frac{1}{2}} \pi^{\frac{1}{2}} (R/8) \int_1^{\sqrt{5}} d\xi \{ \sum_{\nu=0}^{[\frac{1}{2}\ell_3]} \sum_{r=0}^{\ell_3-2\nu+1} \omega_\nu^{\ell_3 0} \, C_r^{\ell_3-2\nu+1} (\kappa R)^r$$

$$\times(1-\xi^2)^r \xi^{\ell_3-2\nu+1-r} \{ 2\xi \int_{\kappa R(\frac{1}{2}-f(\frac{1}{2}))}^{\kappa R(\frac{1}{2}+f(\frac{1}{2}))} \frac{j_{\ell_1}(\frac{1}{2}t) j_{\ell_2}(\frac{1}{2}t)}{t^{r+1}} \, dt$$

$$-(1/\kappa R) \int_{\kappa R(\frac{1}{2}-f(\frac{1}{2}))}^{\kappa R(\frac{1}{2}+f(\frac{1}{2}))} \frac{j_{\ell_1}(\frac{1}{2}t) j_{\ell_2}(\frac{1}{2}t)}{t^r} \, dt \} \}$$

To conclude this section, we note that:

(i) We have reduced the three-dimensional multi-center integrals into a sum of one-dimensional integrals whose integrands involve the sine and cosine integrals. The sine and cosine integrals can be evaluated quickly and accurately and can be called directly from the IBM Scientific Subroutines Package. We shall discuss such evaluations in Appendix G.

(ii) It looks as though the expressions for I_{AA}^i, I_{BB}^i, I_{AB}^i, I_{A0}^i, I_{B0}^i and I_{00}^i are very formidable, yet in the actual calculations they are much more simple. This is because the ℓ-values used in the basis of the MSXα spin-orbitals are usually small, and in most cases, do not exceed 3. Thus, for example, if we use s and p atomic orbitals ($\ell = 0,1$) for the σ state ($m = 0$) in the MSXα calculation, then by equation (4.11),

there is only one term in the summation of ν_1, ν_2 and r since
$(\ell-m)/2 = 0$.

(iii) By partitioning the region of integration into different parts, we can find the contributions to the total force by the electronic charge in each of the regions and for each molecular state:

$$F_{total} = \sum_i n_i F^i + F_N$$
$$= \sum_i n_i (F_A^i + F_B^i + F_{II}^i + F_{out}^i) + F_N$$

where i represents the molecular state i,

F_A^i is the force exerted by the electronic charge inside sphere A for the ith state. Similarly for F_B^i, F_{II}^i and F_{out}^i,

F_N is the force exerted by the other nucleus.

4.5 Results and Discussion

The Hellmann-Feynman force calculations have been carried out for two different systems: the hydrogen molecule and the nitrogen molecule. The hydrogen molecule is investigated because it is the simplest diatomic molecule and accurate results had been previously obtained (see Kolos and Wolniewicz (1964)) so that we can make some comparison. The nitrogen molecule is investigated because its electronic configuration for the ground state is a closed shell configuration in which case the MSXα method should work better. Also, it involves the π-states so that we can see how our

method works for a more complicated case.

Hydrogen molecule: H_2

(A) The ground state for the hydrogen molecule H_2 is $^1\Sigma_g^+$ and the electronic configuration is $1\sigma_g^2$. Forces for three different bond distances are computed in order to plot a force curve and to obtain the equilibrium separation R_e and the force constant k_e. First, for each bond distance, a non-spin-polarized MSXα calculation is carried out by using s and p orbitals in the atomic regions and s and d orbitals in the outer sphere. Then, the electrostatic force is calculated, according to the method described in the previous section, by using the converged wavefunctions. The results are listed in table (4.1), and the curve is plotted in figure (4.4).

(B) In order to check the validity of the Hellmann-Feynman Theorem of the MSXα spin-orbitals, the non-muffin-tin total energy $<E_{x\alpha}(\tilde{\rho})>$ of H_2 is calculated. From the values of $<E_{x\alpha}(\tilde{\rho})>$, we obtain the values of $-\dfrac{\partial <E_{x\alpha}(\tilde{\rho})>}{\partial R}$ at the three different separations by least squares fit. The results are listed in table (4.2). Two such curves are plotted, one for the wavefunction with basis: $\ell=0,1$ in the atomicsphere, $\ell=0,2$ in the outer sphere; another for the wavefunction with basis: $\ell=0$ in the atomic sphere, $\ell=0,2$ in the outer sphere. Also, to compare with the experimental result, a curve with $-\dfrac{\partial E}{\partial R}$ against R where E is the total energy calculated by Kolos and Wolniewicz (see Kolos and Wolniewicz (1964)) is plotted. Such an H_2 calculation is considered to be more accurate

TABLE 4.1

Force Calculations For H_2 ($^1\Sigma_g^+$: $1\sigma_g^2$)

	$2F_A^{\sigma}g$	$2F_B^{\sigma}g$	$2F_{out}^{\sigma}g$	$2F_{II}^{\sigma g}$	F_N	F_{total}
R=1.4	0.264	0.271	-0.026	0.442	-1.020	-0.068
R=1.44	0.262	0.266	-0.026	0.417	-0.965	-0.046
R=1.5	0.257	0.258	-0.025	0.403	-0.889	0.004

* Basis: $\ell=0,1$ in the atomic spheres
       $\ell=0,2$ in the outer sphere.
  $\alpha=0.77627$
  R in atomic unit; F in Rydberg/a.u.

TABLE 4.2

Comparison of F_{total} and $-\dfrac{\partial <E_{x\alpha}(\tilde{\rho})>}{\partial R}$ for H_2

	(a) F_{total}	(b) $-\dfrac{\partial <E_{x\alpha}(\tilde{\rho})>}{\partial R}$	(c) $-\dfrac{\partial <E_{x\alpha}(\tilde{\rho})>}{\partial R}$	(d) $\dfrac{\partial <E>}{\partial R}$
R=1.4	-0.068	-0.024	-0.035	-0.004
R=1.44	-0.046	0.004	-0.012	0.032
R=1.5	0.004	0.046	0.024	0.068
R_e	1.495	1.43	1.46	1.401
k_e	0.72	0.71	0.60	0.73

(a) Hellmann-Feynman Force with basis: $\ell=0,1$ in the atomic region; $\ell=0,2$ in the outer sphere.
(b) Basis: $\ell=0,1$ in the atomic region, $\ell=0,2$ in the outer sphere.
(c) Basis: $\ell=0$ in the atomic region; $\ell=0,2$ in the outer sphere.
(d) Calculated with the Kolos-Wolniewicz wavefunction
Force in Ry/a.u.; R in atomic units; k_e in Ry/a.u.

Fig. 4.4 Force Curves for H_2

1. Basis: $\ell=0,1$ in the H sphere
          $\ell=0,2$ in the outer sphere
2. Basis: $\ell=0$ in the H sphere
          $\ell=0,2$ in the outer sphere.

Force(Ryd/a.u.)

Legend:
- ✕ Experimental
- ⊙ $\frac{\partial E_{x\alpha}(\tilde{\rho})}{\partial R}$ 1
- △ $\frac{\partial E_{x\alpha}(\tilde{\rho})}{\partial R}$ 2
- ▱ $F_{x\alpha}(\tilde{\rho})$

separation(a.u.)
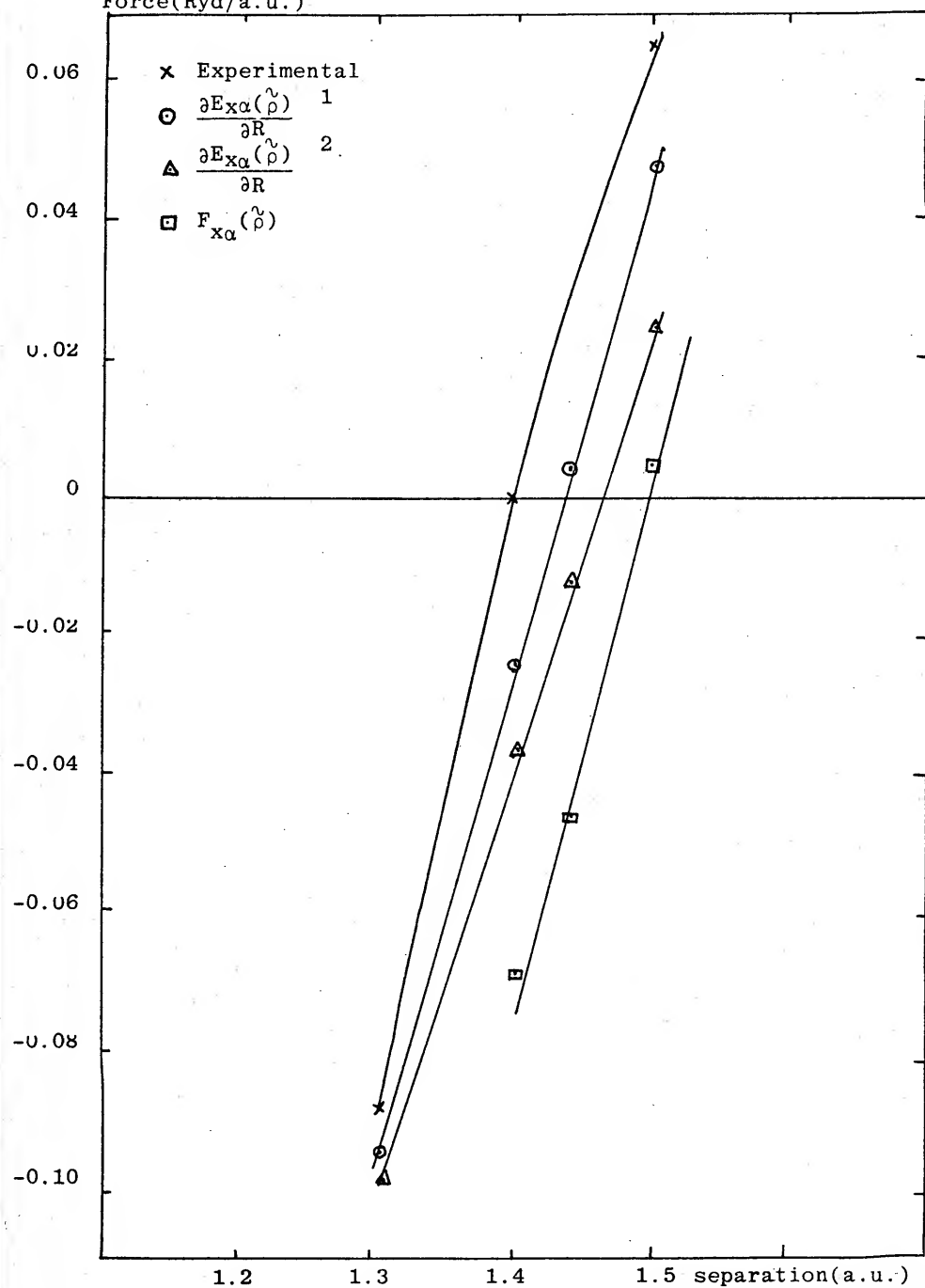
TABLE 4.3

ℓ-Dependence of Hellmann-Feynman Forces for H_2 at R=1.4 a.u.

	$2F_A^{\sigma_g}$	$2F_B^{\sigma_g}$	$2F_{out}^{\sigma_g}$	$2F_{II}^{\sigma_g}$	F_N	F_{total}
#1	0.265	0.271	−0.026	0.442	−1.020	−0.068
#2	0.268	0.274	−0.026	0.442	−1.020	−0.062

#1: ℓ=0,1 in the atomic region; ℓ=0,2 in the outer sphere
#2: ℓ=0,1,2 in the atomic region; ℓ=0,2 in the outer sphere.
Force in Ry/a/u.

than that experimentally observed. The equilibrium separa-
tions R_e and the force constants k_e for each of the curves
are obtained. The results are listed in table (4.2) and the
curves are plotted in figure (4.4).

(C) To check the sensitivity of the force with re-
spect to the basis functions, two different calculations, one
with s, p orbitals in the atomic region while the other with
with s, p, d orbitals (both with s, d functions in the outer
sphere), are carried at R=1.4 a.u. The results are in table
(4.3).

Nitrogen Molecule: N_2

Bader,Henneker and Cade have done some force calcula-
tions by using Hartree-Fock wavefunctions as the basis (see
Bader, Henneker and Cade (1967)). In order to compare these
two methods, a force calculation for nitrogen molecule is
also done by using the MSXα wavefunctions.

Both the MSXα and the Hartree-Fock calculations are
carried out at experimental equilibrium separation R_e=2.07
a.u. The ground state for N_2 is ${}^1\Sigma_g^+$ and the electronic con-
figuration is $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2$. The spin- polarized α value
for nitrogen, α=0.74522 is used, and the ℓ values used for
the different molecular orbitals are listed as in table (4.4).
Here we treat the $1\sigma_g$ and $1\sigma_u$ as core states. The results of
the force calculations are as in table(4.5).

Discussion :

When we compare $F_{x\alpha}(\bar{\rho})$, $F_{x\alpha}(\overset{\sim}{\rho})$ and the experimental
values for the force, we find that we have achieved a big

TABLE 4.4

ℓ-Values in the MSXα Calculation for N_2 ($^1\Sigma_g^+$)

	$2\sigma_g$	$2\sigma_u$	$1\pi_u$	$3\sigma_g$
atomic	0,1,2	0,1,2	1,2	0,1,2
outer	0,2	1,3	1,3	0,2

* $1\sigma_g$ and $1\sigma_u$ are both treated as core states.

TABLE 4.5

Hellmann–Feynman Forces for N_2 at R=2 a.u.
Calculated with MSXα and Hartree–Fock Wavefunctions

	$1\sigma_g^2 1\sigma_u^2$	$2\sigma_g^2$	$2\sigma_u^2$	$1\pi_u^4$	$3\sigma_g^2$
f_A *	0.	1.513	−0.501	1.278	0.462
f_B	7.	2.227	0.952	2.317	1.685
f_{out}	0.	0.003	−0.844	0.160	−0.788
f_{II}	0.	3.316	−0.003	3.274	0.452
$f_{x\alpha}$	7.	7.059	−0.395	7.029	1.811
$f_{Har-Fock}$	7.858	9.387	−1.621	8.512	0.525

$F_{total}(\tilde{\rho}_{x\alpha}) = -1.996$

$F_{total}(\text{Hartree-Fock}) = -0.263$

* Total electronic force
Force in Ry/a.u.

improvement by using the non-muffin-tin charge density to calculate the force. The force constant k_e and the equilibrium separation for H_2 calculated with this method involve errors of 1.4% and 7% respectively, while the $F_{X\alpha}(\bar{\rho})$ indicates no binding at all.

However, when we compare $F_{X\alpha}(\overset{\curvearrowright}{\rho})$ and $-\dfrac{\partial E_{X\alpha}(\overset{\curvearrowright}{\rho})}{\partial R}$, we find that there is some difference between them. This means that the Hellmann-Feynman Theorem is not quite correct with the approximate MSXα wavefunctions. Some reasons may be:

(1) Since the wavefunctions we used are not exact solutions to the Xα Schrödinger equations. It also assumes the muffin-tin potential approximation and the potential is generated only from a muffin-tin averaged charge density. Thus, it is only an approximate Xα wavefunction and we cannot claim that it should satisfy the Hellman-Feynman Theorem very well. Actually, due to the polarization effect, the potential on both sides of the atomic spheres should be different. The potential in the bonding region facing the other nucleus should be less shallow than the potential in the outer region. Thus, there should be more charge in the bonding region than what is expected by using the muffin-tin averaged potential. This means that the actual force should be more attractive than the force we got by assuming the muffin-tin potential. This polarization effect should be especially severe for the core state, for which the electronic charge accumulates near the nucleus.

(2) Besides assuming the muffin-tin averaged poten-
tial, we also use only a finite set of basis functions with
small ℓ values. This may not be important in calculating
the total energy but it may be important in calculating the
force, because the force is much more sensitive to the wave-
function than the total energy is. We further note that:

(i) In the force calculation for the hydrogen mole-
cule (table (4.2) and figure (4.4)), the values of $F_{x\alpha}(\tilde{\rho})$
by using the basis ($\ell_H=0,1$; $\ell_{out}=0,2$)are closer to the values
of $\frac{\partial E_{x\alpha}(\tilde{\rho})}{\partial R}$ calculated with the basis ($\ell_H=0$; $\ell_{out}=0,2$) than
to that obtained with the basis ($\ell_H=0,1$; $\ell_{out}=0,2$). Further-
more, we have the following relation:

$$F_{x\alpha}(\tilde{\rho})\ (\ell_H=0,1;\ \ell_{out}=0,2)\ <\ \frac{\partial E_{x\alpha}(\tilde{\rho})}{\partial R}\ (\ell_H=0;\ \ell_{out}=0,2)$$

$$<\ \frac{\partial E_{x\alpha}(\tilde{\rho})}{\partial R}\ (\ell_H=0,1;\ \ell_{out}=0,2)\ <\ F_{experimental}$$

This can be expected since if the error in $F_{x\alpha}(\tilde{\rho})$ ($\ell_H=0,1$;
$\ell_{out}=0,2$) is of first order of the errror in the wavefunction,
then the error in $E_{x\alpha}(\tilde{\rho})$ ($\ell_H=0,1$; $\ell_{out}=0,2$) is of second
order and that the error in $E_{x\alpha}(\tilde{\rho})$ ($\ell_H=0$; $\ell_{out}=0,2$) should
be larger than that of $E_{x\alpha}(\tilde{\rho})$($\ell_H=0,1$; $\ell_{out}=0,2$) but smaller
than second order.

(ii) In table (4.3), we see that when we increase
the ℓ-values, the net force becomes less repulsive and agrees
better with $\frac{\partial E_{x\alpha}(\tilde{\rho})}{\partial R}$. The improvement is very slight. However,
if we use only s orbitals in the atomic spheres, then $F_A=0$

and the net force becomes more repulsive. Thus, the p orbital is very important in the force calculations, although the s orbital is almost sufficient for the total energy calculation.

In the force calculation for the nitrogen molecule, we see that the MSXα forces have the same characteristic as the Hartree-Fock forces. Again, the MSXα forces are too repulsive. However, the relative values of forces contributed by the different molecular states for both cases are comparable, and the σ_u state in both calculations contributes repulsive force. Of course, we should not expect our result could be the same as that of the Hartree-Fock calculation. What we should expect is just a general characteristic of these two kinds of forces.

In conclusion, the use of MSXα wavefunctions instead of the muffin-tin averaged charge density to calculate the force makes a big improvement. It gives a reasonable equilibrium separation and a good force constant. However, due to the muffin-tin potential and the truncation of ℓ-values in the basis set, the existing calculation of MSXα wavefunctions still has to be modified to satisfy the Hellmann-Feynman Theorem.

CHAPTER V

DIPOLE MOMENT CALCULATIONS

5.1 Introduction

In Chapter III,we have discussed how to compute the
dipole moment of a diatomic molecule by assuming the muffin-
tin charge density. In this chapter, we shall discuss the
same calculation but using the non-muffin-tin charge density,
i.e., the charge density formed from the MSXα wavefunctions.
We shall first discuss the computational procedure and then
give the results for some diatomic molecules. The results
show that the use of non-muffin-tin charge density indeed
provides big improvements over the use of muffin-tin charge
density.

5.2 Method of Dipole Moment Calculations

To calculate the dipole moment of a diatomic mole-
cule, we need to evaluate the integral $\int \rho(\vec{r})z \, d^3r$ contrib-
uted by the electronic cloud. Again, in the MSXα calcula-
tions, we have:

$$\rho(\vec{r}) = \sum_i n_i \, \tilde{u}_i^*(\vec{r}) \, \tilde{u}_i(\vec{r})$$

As usual, we partition the coordinate space into three re-
gions: the atomic region, the intersphere region, and the
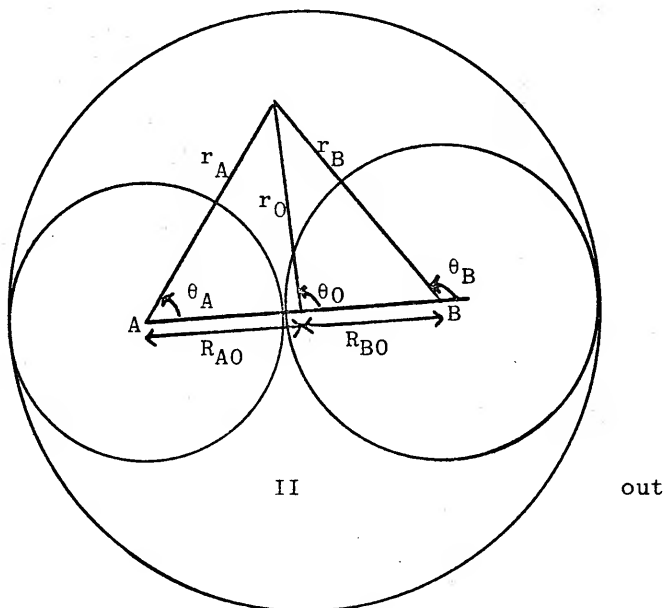
Fig. 5.1   Schematic Representation of A Heteronuclear
Diatomic Molecule in the MSXα Calculation.

outer sphere region (figure 5.1). As we have mentioned in Chapter III, the value of the dipole moment is independent of the choice of the origin for a neutral molecule, we can choose the center of the outer sphere as the origin. Then we have:

$$\int \rho(\vec{r})z_0 \; d^3r = \sum_i n_i \; (\mu_A^i + \mu_B^i + \mu_{out}^i + \mu_{II}^i) \qquad (5.1)$$

where

$$\mu_A^i = \int_A \tilde{u}_i^*(\vec{r})\tilde{u}_i(\vec{r})z_0 \; d^3r$$

$$\mu_B^i = \int_B \tilde{u}_i^*(\vec{r})\tilde{u}_i(\vec{r})z_0 \; d^3r$$

$$\mu_{out}^i = \int_{out} \tilde{u}_i^*(\vec{r})\tilde{u}_i(\vec{r})z_0 \; d^3r$$

$$\mu_{II}^i = \int_{II} \tilde{u}_i^*(\vec{r})\tilde{u}_i(\vec{r})z_0 \; d^3r$$

and the dipole moment μ is: $\qquad \mu = \mu_N - \mu_e$

where $\mu_N = Z_B R_{B0} - Z_A R_{A0}$ is the nuclear contribution,

$\mu_e = \int \rho(\vec{r})z_0 \; d^3r$ is the electronic contribution,

Z_A, Z_B are respectively the atomic numbers of the two nuclei A and B; μ is in atomic units.

Integral Over Sphere A: μ_A^i

Inside sphere A, we have:

$$\tilde{u}_i(\vec{r}) = \sum_{\ell} C^{iA}_{\ell m} R_\ell(r_A) Y^m_\ell(\vec{r}_A)$$

and
$$z_0 = z_A - R_{A0} = (4\pi/3)^{\frac{1}{2}} r_A Y^0_1(\vec{r}_A) - R_{A0}$$

Thus, we have:

$$\mu^i_A = \int_A \tilde{u}_i(\vec{r}) \, \tilde{u}_i(\vec{r}) \, z_0 \, d^3r$$

$$= \sum_{\ell_1} \sum_{\ell_2} C^{iA}_{\ell_1 m} C^{iA}_{\ell_2 m} \int_A R_{\ell_1}(r_A) Y^m_{\ell_1}(\vec{r}_A) R_{\ell_2}(r_A) Y^m_{\ell_2}(\vec{r}_A)$$

$$\times \{ (4\pi/3)^{\frac{1}{2}} r_A Y^0_1(\vec{r}_A) - R_{A0} \} \, d^3r$$

$$= \sum_{\ell_1} \sum_{\ell_2} C^{iA}_{\ell_1 m} C^{iA}_{\ell_2 m} \{ (4\pi/3)^{\frac{1}{2}} I(\ell_1, m; \ell_2, m; 1, 0)$$

$$\times \int_o^{R_A} R_{\ell_1}(r_A) R_{\ell_2}(r_A) r^3_A \, dr_A$$

$$- R_{A0} \, \delta_{\ell_1 \ell_2} \int_o^{R_A} R_{\ell_1}(r_A) R_{\ell_2}(r_A) r^2_A \, dr_A \}$$

Integral Over Sphere B: μ^i_B

Inside sphere B, we have

$$\tilde{u}_i(\vec{r}) = \sum_{\ell} C^{iB}_{\ell m} R_\ell(r_B) Y^m_\ell(\vec{r}_B)$$

and
$$z_0 = z_B + R_{B0} = (4\pi/3)^{\frac{1}{2}} r_B Y^0_1(\vec{r}_B) + R_{B0}$$

Thus, we have:

$$\mu_B^i = \int_B \tilde{u}_i^*(\vec{r}) \, \tilde{u}_i(\vec{r}) \, z_0 \, d^3r$$

$$= \sum_{\ell_1} \sum_{\ell_2} C_{\ell_1 m}^{iB} \dot{C}_{\ell_2 m}^{iB} \quad (4\pi/3)^{\frac{1}{2}} \, I(\ell_1, m; \ell_2, m; 1, 0)$$

$$\times \int_0^{R_B} R_{\ell_1}(r_B) R_{\ell_2}(r_B) r_B^3 \, dr_B + R_{B0} \delta_{\ell_1 \ell_2} \int_0^{R_B} R_{\ell_1}(r_B) R_{\ell_2}(r_B) r_B^2 dr_B \}$$

Integral Over the Outer Sphere: μ_{out}^i

Inside the outer sphere, we have:

$$\tilde{u}_i(\vec{r}) = \sum_\ell C_{\ell m}^{i0} R_\ell(r_0) Y_\ell^m(\vec{r}_0)$$

Thus $\mu_{out}^i = \int_{out} \tilde{u}_i^*(\vec{r}) \, \tilde{u}_i(\vec{r}) \, z_0 \, d^3r$

$$= \sum_{\ell_1} \sum_{\ell_2} C_{\ell_1 m}^{i0} C_{\ell_2 m}^{i0} \int_{out} R_{\ell_1}(r_0) Y_{\ell_1}^m(\vec{r}_0) R_{\ell_2}(r_0) Y_{\ell_2}^m(\vec{r}_0)$$

$$\times (4\pi/3)^{\frac{1}{2}} r_0 Y_1^0(\vec{r}_0) \, d^3r$$

$$= \sum_{\ell_1} \sum_{\ell_2} C_{\ell_1 m}^{i0} C_{\ell_2 m}^{i0} \, (4\pi/3) \quad I(\ell_1, m; \ell_2, m; 1, 0)$$

$$\times \int_{R_{out}}^\infty R_{\ell_1}(r_0) R_{\ell_2}(r_0) r_0^3 \, dr_0$$

Integral Over the Intersphere Region: μ_{II}^i

In the intersphere region, we can express $\tilde{u}_i(\vec{r})$ as linear combinations of products of Neumann functions and spherical harmonics as discussed in the force calculations. In the same way as before, we obtain:

$$\mu_{II}^i = \int_{II} \tilde{u}_i^*(\vec{r}) \, \tilde{u}_i(\vec{r}) \, z_0 \, d^3r$$

$$= \sum_{\ell_1,\ell_2} A_{\ell_1 m}^{iA} A_{\ell_2 m}^{iA} \, I_{AA}(\ell_1,\ell_2,m) + \sum_{\ell_1,\ell_2} A_{\ell_1 m}^{iB} A_{\ell_2 m}^{iB} \, I_{BB}(\ell_1,\ell_2,m)$$

$$+ \sum_{\ell_1,\ell_2} A_{\ell_1 m}^{i0} A_{\ell_2 m}^{i0} \, I_{00}(\ell_1,\ell_2,m) + 2 \sum_{\ell_1,\ell_2} A_{\ell_1 m}^{iA} A_{\ell_2 m}^{iB} I_{AB}(\ell_1,\ell_2,m)$$

$$+2 \sum_{\ell_1,\ell_2} A_{\ell_1 m}^{iA} A_{\ell_2 m}^{i0} \, I_{A0}(\ell_1,\ell_2,m) + 2 \sum_{\ell_1,\ell_2} A_{\ell_1 m}^{iB} A_{\ell_2 m}^{i0} I_{B0}(\ell_1,\ell_2,m)$$

$$(5.2)$$

where $I_{AA}(\ell_1,\ell_2,m) = \int_{II} \eta_{\ell_1}(\kappa r_A) Y_{\ell_1}^m(\vec{r}_A) \eta_{\ell_2}(\kappa r_A) Y_{\ell_2}^m(\vec{r}_A) z_0 d^3r$

$$I_{BB}(\ell_1,\ell_2,m) = \int_{II} \eta_{\ell_1}(\kappa r_B) Y_{\ell_1}^m(\vec{r}_B) \eta_{\ell_2}(\kappa r_B) Y_{\ell_2}^m(\vec{r}_B) z_0 d^3r$$

$$I_{AB}(\ell_1,\ell_2,m) = \int_{II} \eta_{\ell_1}(\kappa r_A) Y_{\ell_1}^m(\vec{r}_A) \eta_{\ell_2}(\kappa r_B) Y_{\ell_2}^m(\vec{r}_B) z_0 d^3r$$

$$I_{A0}(\ell_1,\ell_2,m) = \int_{II} \eta_{\ell_1}(\kappa r_A) Y_{\ell_1}^m(\vec{r}_A) j_{\ell_2}(\kappa r_0) Y_{\ell_2}^m(\vec{r}_0) z_0 d^3r$$

$$I_{B0}(\ell_1,\ell_2,m) = \int_{II} \eta_{\ell_1}(\kappa r_B) Y_{\ell_1}^m(\vec{r}_B) j_{\ell_2}(\kappa r_0) Y_{\ell_2}^m(\vec{r}_0) z_0 d^3r$$

$$I_{00}(\ell_1,\ell_2,m) = \int_{II} j_{\ell_1}(\kappa r_0) Y_{\ell_1}^m(\vec{r}_0) j_{\ell_2}(\kappa r_0) Y_{\ell_2}^m(\vec{r}_0) z_0 d^3r$$

To evaluate the above integrals, again we employ the Prolate Spheroidal Coordinates as we did in the force calculations. However, since in this case we have a heteronuclear diatomic case, so the limits of integration when transformed to Prolate Spheroidal Coordinates would become more complex. We shall discuss each of the integrals in the following:

(1) I_{AA}: $\displaystyle\int_{II} \eta_{\ell_1}(\kappa r_A) Y_{\ell_1}^m(\vec{r}_A) \eta_{\ell_2}(\kappa r_A) Y_{\ell_2}^m(\vec{r}_A) z_0 \, d^3r$

This is a two-center integral. We shall express the integrand in terms of Prolate Spheroidal Coordinates with A and 0 as the two foci (figure(5.1)):

$$\xi = (r_A + r_0)/R_{A0}$$

$$\eta = (r_A - r_0)/R_{A0}$$

$$\phi = \phi_A = \phi_0$$

The reciprocal relations are:

$$\mathbf{r}_A = \tfrac{1}{2} R_{A0}\,(\xi + \eta) \qquad\qquad r_0 = \tfrac{1}{2} R_{A0}\,(\xi - \eta)$$

$$\cos\Theta_A = (1+\xi\eta)/(\xi+\eta) \qquad \text{and} \qquad \cos\Theta_0 = -\,(1-\xi\eta)/(\xi-\eta)$$

$$\sin\Theta_A = \frac{\{(\xi^2-1)(1-\eta^2)\}^{\frac{1}{2}}}{\xi+\eta} \qquad\qquad \sin\Theta_0 = \frac{\{(\xi^2-1)(1-\eta^2)\}^{\frac{1}{2}}}{\xi-\eta}$$

$$(5.3)$$

and the volume element is:

$$d^3r = (\tfrac{1}{2} R_{A0})^3\,(\xi^2 - \eta^2)\, d\xi\, d\eta\, d\phi$$

Since the two atomic spheres are in general of different size, the geometry of the partition is a function of

two parameters, the bond distance R and the ratio of the radii of any two spheres, in this case, we choose $\beta = R_B/R$. Then we can express the different quantities in terms of these two parameters:

$R_A = (1-\beta)/R$: $R_B = \beta R$; $R_{out} = R$; $R_{A0} = \beta R$;

$R_{B0} = (1-\beta)/R$ \hfill (5.4)

With the coordinate system as expressed in equation (5.3) and also by the relations in (5.4), we have the following restrictions for the intersphere region:

(1) $r_A \geq R_A$

implies $\frac{1}{2}R_{A0}(\xi+\eta) \geq R_A$ or $\xi+\eta \geq 2(1-\beta)/\beta$

(2) $r_0 \leq R_{out}$

implies $\frac{1}{2}R_{A0}(\xi+\eta) \leq R_{out}$ or $\xi-\eta \leq 2/\beta$

(3) $r_B \geq R_B$

and $r_B^2 = r_A^2 + R^2 - 2r_A R\cos\Theta_A$

implies $\eta^2 - \frac{4}{\beta}(1-\frac{1}{2}\beta)\xi\eta + \xi^2 - \frac{4}{\beta}(\beta^2+\beta-1) \geq 0$

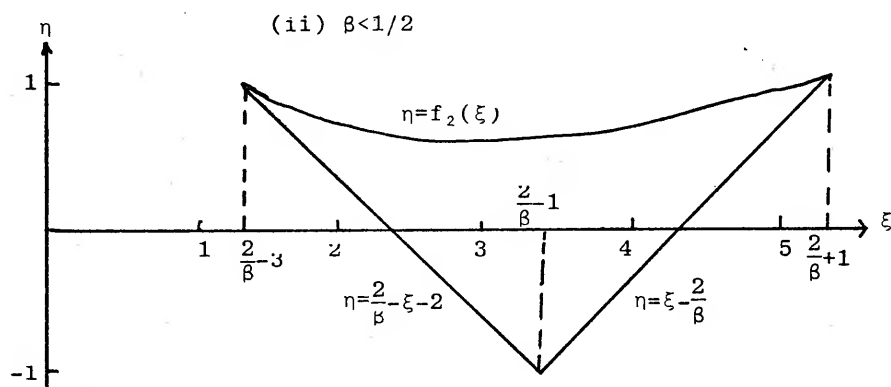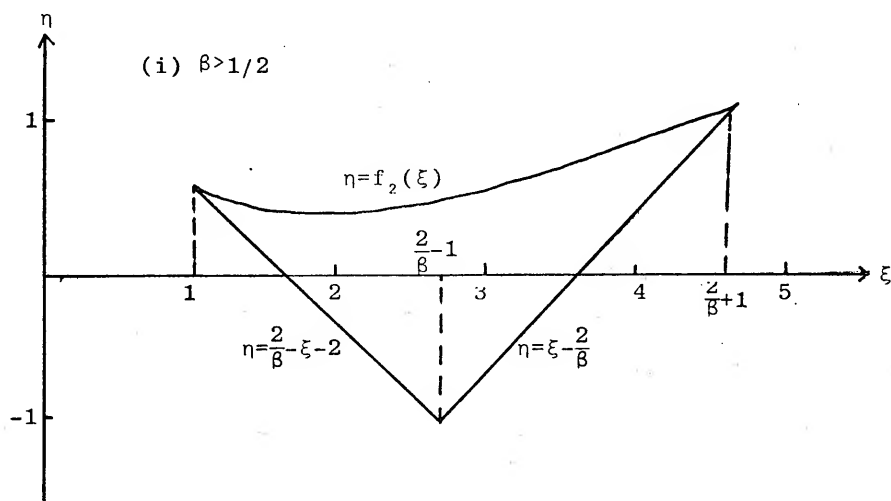(4) $\xi \geq 1$

(5) $-1 \leq \eta \leq 1$

Fig. 5.2 Boundary of the Intersphere Region in Prolate
          Spheroidal Coordinates with A and O as the Foci.

Combining (1), (2), (3), (4) and (5), we have the transformed region as defined by the following limits (figure 5.2):

$$\xi \geqslant \xi_0 = \begin{cases} 1 & \text{if} \quad \beta \geqslant \frac{1}{2} \\ \\ \frac{2}{\beta} - 3 & \text{if} \quad \beta < \frac{1}{2} \end{cases}$$

$$\xi \leqslant \frac{2}{\beta} + 1$$

$$f_1(\xi) \leqslant \eta \leqslant f_2(\xi)$$

where
$$f_2(\xi) = \frac{2}{\beta}\{(1-\tfrac{1}{2}\beta)\xi - \{(1-\beta)\xi^2 + (\beta^2+\beta-1)\}^{\frac{1}{2}}\}$$

and
$$f_1(\xi) = \begin{cases} 2/\beta - 2 - \xi & \text{if} \quad \xi < 2/\beta - 1 \\ \\ \xi - 2/\beta & \text{if} \quad \xi > 2/\beta - 1 \end{cases}$$

Expanding the spherical harmonics and the Neumann functions in terms of ξ, η, ϕ as we did in the force calculation in Chapter IV, we have the following result after some straightforward algebra:

$$I_{AA} = N_{\ell_1}^m \, N_{\ell_2}^m \, (-1)^{\ell_1+\ell_2+1} (R_{A0}/2)^4 \int_{\frac{2}{\beta}}^{\frac{2}{\beta}+1} d\xi \sum_{r=0}^{m} \sum_{\nu_1=0}^{[\frac{1}{2}(\ell_1-m)]} \sum_{\nu_2=0}^{[\frac{1}{2}(\ell_2-m)]}$$

$$\sum_{s=0}^{\ell_1+\ell_2-2m-2\nu+2r} \{(-1)^r \, \omega_{\nu_1}^{\ell_1 m} \, \omega_{\nu_2}^{\ell_2 m} \, C_r^m \, C_s^{\ell_1+\ell_2-2m-2\nu+2r} \, (\, R_{A0})^{s-2}$$

$$\times\ 2(1-\xi^2)^s\ \ \xi^{\ell_1+\ell_2-2m-2\nu+2r-s}\ \{2\xi(1+\xi^2)\ h^1_{\ell_1\ell_2}(s+1,\xi)$$

$$-\ \frac{3\xi^2+1}{R_{A0}}\ h^1_{\ell_1\ell_2}(s,\xi)\ +\ \xi/(\kappa R_{A0})^2\ h^2_{\ell_1\ell_2}(s-1,\xi)\}\}$$

where $\nu = \nu_1 + \nu_2$

and the h^1-functions are defined as:

$$h^1_{\ell_1\ell_2}(s,\xi)\ =\ \sum_{u=0}^{1}\ \sum_{v=0}^{1}\ \sum_{n=0}^{[\frac{1}{2}(\ell_1-u)]+[\frac{1}{2}(\ell_2-v)]}\ (-1)^{u+v}\ A_n^{(u,v)}$$

$$\times\ Q^{(u,v,1)}_{\ell_1\ell_2}(s+2n+u+v,\xi)$$

where the A-coefficients are also defined in Chapter IV and the Q-functions are defined in terms of sine and cosine integrals, similarly to the corresponding terms in the force calculations except for the integration limits:

$$Q^{(u,v,1)}_{\ell_1\ell_2}(\ell,\xi)\ =\ \{\ \cos\tfrac{1}{2}(\ell_1+\ell_2)\pi\ (\delta_{u+v,0}-\delta_{u+v,2})$$

$$+\ \sin\tfrac{1}{2}(\ell_1+\ell_2)\pi\ \delta_{u+v,1}\}\int_{\kappa R(\zeta+f_1(\zeta))}^{\kappa R(\zeta+f_2(\zeta))}\ \frac{\cos t}{t^\ell}\ dt$$

$$+\ \{\sin\tfrac{1}{2}(\ell_1+\ell_2)\pi\ (\delta_{u+v,2}-\delta_{u+v,0})$$

$$+\ \cos\tfrac{1}{2}(\ell_1+\ell_2)\pi\ \delta_{u+v,1}\}\int_{\kappa R(\zeta+f_1(\zeta))}^{\kappa R(\zeta+f_2(\zeta))}\ \frac{\sin t}{t^\ell}dt$$

$$+\ \{\sin\tfrac{1}{2}(\ell_1-\ell_2)\pi\ \delta_{u+v,1}(\delta_{v0}-\delta_{v1})$$

$$+\ \cos\tfrac{1}{2}(\ell_1-\ell_2)\pi\ (\delta_{u+v,0}\ \delta_{u+v,2})\}\int_{\kappa R(\zeta+f_1(\zeta))}^{\kappa R(\zeta+f_2(\zeta))}\ \frac{dt}{t^\ell}$$

(2) I_{A0}: $\int_{II} \eta_{\ell_1}(\kappa r_A) Y_{\ell_1}^m(\vec{r}_A) j_{\ell_2}(\kappa r_0) Y_{\ell_2}^m(\vec{r}_0) z_0 d^3r$

This is also a two-center integrals, we can use the same coordinate system as in the evaluation of I_{AA}. The result is:

$$I_{AA} = N_{\ell_1}^m N_{\ell_2}^m (-1)^{\ell_1} (R_{A0}/2)^4 (\kappa R_{A0})^{-3} \int_{j_0}^{\frac{2}{\beta}+1} d\xi \sum_{u=0}^{m} \sum_{v=0}^{2u} \sum_{\nu_1=0}^{[\frac{1}{2}(\ell_1-m)]}$$

$$\sum_{r=0}^{\ell_1-m-2\nu_1} \sum_{\nu_2=0}^{[\frac{1}{2}(\ell_2-m)]} \sum_{s=0}^{\ell_2-m-2\nu_2} \{(-1)^{u+v} \omega_{\nu_1}^{\ell_1 m} \omega_{\nu_2}^{\ell_2 m} (-1)^{\ell_2-2\nu_2}$$

$$\times C_u^m C_v^{2u} C_r^{\ell_1-m-2\nu_1} C_s^{\ell_2-m-2\nu_2} 2(\kappa R_{A0})^{\ell_1-2\nu_1-2u+v-r+\ell_2-2\nu_2-s}$$

$$\times (1-\xi^2)^{\ell_1-m-2\nu_1-r+\ell_2-2\nu_2-s} \xi^{v+r+s} \{(1+\xi^2)$$

$$\times h_{\ell_1\ell_2}^2(\ell_1-2\nu_1-2u+v-r, \ell_2-2\nu_2-s, \xi) - \xi/(\kappa R_{A0})$$

$$\times h_{\ell_1\ell_2}^2(\ell_1-2\nu_1-2u+v-r-1, \ell_2-2\nu_2-s, \xi)\}\}$$

where $h_{\ell_1\ell_2}^2(\ell_3, \ell_4, \xi) = \sum_{u=0}^{1} \sum_{v=0}^{1} \sum_{k_1=0}^{[\frac{1}{2}(\ell_1-u)]} \sum_{k_2=0}^{[\frac{1}{2}(\ell_2-v)]}$

$$\{ (-1)^{u+k_1+k_2}(\ell_1+\tfrac{1}{2}, 2k_1+u)(\ell_2+\tfrac{1}{2}, 2k_2+v)$$

$$\times Q_{\ell_1\ell_2}^{(u,v,2)}(\ell_3+2k_1+u, \ell_4+2k_2+v, \xi) \}$$

and the Q-functions are defined by:

$$Q_{\ell_1\ell_2}^{(u,v,2)}(p,q,\xi) = \{\sin(\kappa R_{A0}\xi-\tfrac{1}{2}(\ell_1-\ell_2)\pi)\ (\delta_{u+v,0}-\delta_{u+v,2})$$

$$+ \cos(\kappa R_{A0}\xi-\tfrac{1}{2}(\ell_1-\ell_2)\pi)\ \delta_{u+v,1}\}$$

$$\times \int_{\kappa R_{A_0}(\xi+f_1(\xi))}^{\kappa R_{A_0}(\xi+f_2(\xi))} \frac{\cos t}{t^p(2\kappa R_{A0}\xi-t)^q}\,dt$$

$$+\{\cos(\kappa R_{A0}\xi-\tfrac{1}{2}(\ell_1-\ell_2)\pi)\ (\delta_{u+v,2}-\delta_{u+v,0})$$

$$+ \sin(\kappa R_{A0}\xi-\tfrac{1}{2}(\ell_1-\ell_2)\pi)\ \delta_{u+v,1}\}$$

$$\times \int_{\kappa R_{A_0}(\xi+f_1(\xi))}^{\kappa R_{A_0}(\xi+f_2(\xi))} \frac{\sin t}{t^p(2\kappa R_{A0}\xi-t)^q}\,dt$$

$$+\{\sin(\kappa R_{A0}\xi+\tfrac{1}{2}(\ell_1+\ell_2)\pi)\ (\delta_{u+v,0}+\delta_{u+v,2})$$

$$+ \cos(\kappa R_{A0}\xi+\tfrac{1}{2}(\ell_1+\ell_2)\pi)\ \delta_{u+v,1}(\delta_{u0}-\delta_{u1})\}$$

$$\times \int_{\kappa R_{A_0}(\xi+f_1(\xi))}^{\kappa R_{A_0}(\xi+f_2(\xi))} \frac{1}{t^p(2\kappa R_{A0}\xi-t)^q}\,dt$$

(3) I_{BB}: $\int_{II}\eta_{\ell_1}(\kappa r_B)Y_{\ell_1}^m(\vec{r}_B)\eta_{\ell_2}(\kappa r_B)Y_{\ell_2}^m(\vec{r}_B)z_0\,d^3r$

This is also a two-center integral. We treat this integral by considering the Prolate Spheroidal Coordinates with 0 and B as the two foci:

$$\xi = (r_0 + r_B)/R_{B0}\ , \quad \eta = (r_0 - r_B)/R_{B0}\ , \quad \phi = \phi_0 = \phi_B\ .$$

With this coordinate system, we have the following restric-

tion for the intersphere region:

(1) $r_B \geqslant R_B$.

implies $(R_{B0}/2)(\xi - \eta) \geqslant R_B$ or $\xi - \eta \geqslant 2\beta/(1 - \beta)$

(2) $r_0 \leqslant R_{out}$

implies $(R_{B0}/2)(\xi + \eta) \leqslant R_{out}$ or $\xi + \eta \leqslant 2/(1 - \beta)$

(3 $r_A \geqslant R_A$

and $r_A^2 = r_B^2 + R^2 + 2r_B R \cos\Theta_B$

implies $\eta^2 + \dfrac{4}{\gamma} (1 - \dfrac{\gamma}{2}) \xi\eta + \xi^2 + \dfrac{4}{\gamma} (1 - \gamma - \gamma^2) \geqslant 0$

where $\gamma = 1-\beta = R_A/R$

(4) $\xi \geqslant 1$

(5) $-1 \leqslant \eta \leqslant 1$

Combining all the above restrictions, we have the transformed region as defined by the following (figure 5.3):
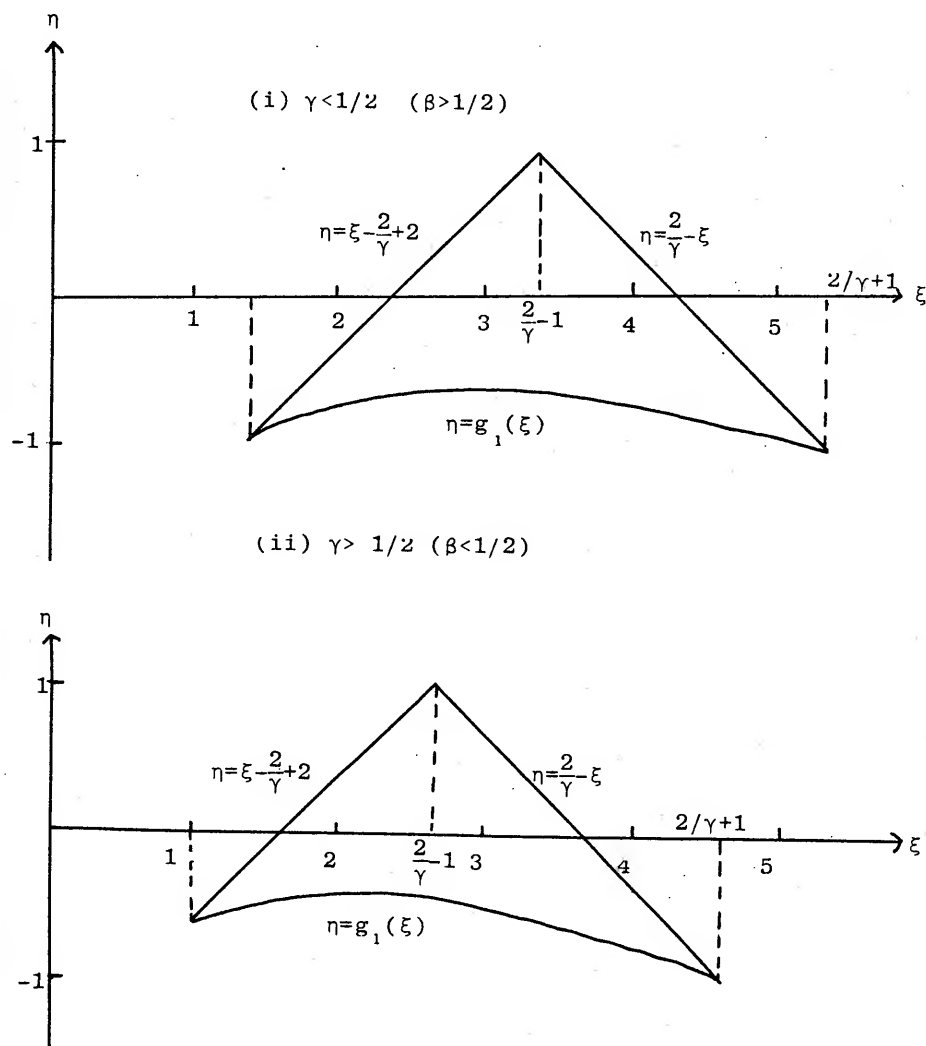
Fig. 5.3 Boundary of the Intersphere Region in
          Prolate Spheroidal Coordinates with O
          and B as the Foci.

$$\xi \geqslant \xi_0' = \begin{cases} 2/\gamma - 3 & \text{if } \gamma < \frac{1}{2} \ (\beta > \frac{1}{2}) \\ \\ 1 & \text{if } \gamma \geqslant \frac{1}{2} \ (\beta \leqslant \frac{1}{2}) \end{cases}$$

$$\xi \leqslant 2/\gamma + 1$$

$$g_1(\xi) \leqslant \eta \leqslant g_2(\xi)$$

where $\quad g_1(\xi) = \frac{2}{\gamma} \{- (1-\gamma/2)\xi + ((1-\gamma)\xi^2 - (1-\gamma-\gamma^2))^{\frac{1}{2}}\}$

$$g_2(\xi) = \begin{cases} \xi - 2/\gamma + 2 & \text{if } \xi < 2/\gamma - 1 \\ \\ 2/\gamma - \xi & \text{if } \xi > 2/\gamma - 1 \end{cases}$$

Expanding the spherical harmonics and the Neumann functions in ξ, η, ϕ, we have the following expression for I_{BB}:

$$I_{BB} = N_{\ell_1}^m N_{\ell_2}^m (-1)^{\ell_1+\ell_2+1} (R_{B0}/2)^4 \int_{\xi_0'}^{\frac{2}{\gamma}+1} d\xi \left\{ \sum_{r=0}^{m} \sum_{\nu_1=0}^{[\frac{1}{2}(\ell_1-m)]} \right.$$

$$\sum_{\nu_2=0}^{[\frac{1}{2}(\ell_2-m)]} \sum_{s=0}^{\ell_1+\ell_2-2m+2r-2\nu} (-1)^{\ell_1+\ell_2-2m+3r-2\nu} \omega_{\nu_1}^{\ell_1 m} \omega_{\nu_2}^{\ell_2 m}$$

$$\times C_r^m C_s^{\ell_1+\ell_2-2m+2r-2\nu} 2(\kappa R_{B0})^{s-2} \xi^{\ell_1+\ell_2-2m+2r-2\nu-s}$$

$$\times (1-\xi^2)^s \left\{ 2\xi(1+\xi^2) h_{\ell_1\ell_2}^3(s+1,\xi) - \frac{3\xi^2+1}{R_{B0}} h_{\ell_1\ell_2}^3(s,\xi) \right.$$

$$\left. + \xi/(\kappa R_{B0})^2 h_{\ell_1\ell_2}^3(s-1,\xi) \right\}\}$$

where $\nu = \nu_1 + \nu_2$

and the h^3-functions are defined as:

$$h^3_{\ell_1\ell_2}(s,\xi) = \sum_{u=0}^{1} \sum_{v=0}^{1} \sum_{n=0}^{[\frac{1}{2}(\ell_1-u)]+[\frac{1}{2}(\ell_2-v)]} (-1)^{u+v} A_n^{(u,v)} Q^{(u,v,3)}_{\ell_1\ell_2}(s+2n+u+v,\xi)$$

where the A-coefficients are defined as before and the Q-functions are defined as below:

$$Q^{(u,v,3)}_{\ell_1\ell_2}(\ell,\xi) = \{ \cos\tfrac{1}{2}(\ell_1+\ell_2)\pi \, (\delta_{u+v,0} - \delta_{u+v,2})$$

$$+ \sin\tfrac{1}{2}(\ell_1+\ell_2)\pi\delta_{u+v,1} \int_{\kappa R_{B0}(\} - \partial_1(\}))}^{\kappa R_{B0}(\} - \partial_2(\}))} \frac{\cos t}{t^\ell} \, dt$$

$$+ \{\sin\tfrac{1}{2}(\ell_1+\ell_2)\pi \, (\delta_{u+v,2} - \delta_{u+v,0})$$

$$+ \cos\tfrac{1}{2}(\ell_1+\ell_2)\pi\delta_{u+v,1}\} \int_{\kappa R_{B0}(\} - \partial_1(\}))}^{\kappa R_{B0}(\} - \partial_2(\}))} \frac{\sin t}{t^\ell} \, dt$$

$$+ \{\cos\tfrac{1}{2}(\ell_1-\ell_2)\pi \, (\delta_{u+v,0} + \delta_{u+v,2})$$

$$+ \sin\tfrac{1}{2}(\ell_1-\ell_2)\pi \, \delta_{u+v,1}(\delta_{v0} - \delta_{v1})\} \int_{\kappa R_{B0}(\} - \partial_1(\}))}^{\kappa R_{B0}(\} - \partial_2(\}))} \frac{dt}{t^\ell}$$

(4) I_{B0}: $\displaystyle\int_{II} \eta_{\ell_1}(\kappa r_B) Y^m_{\ell_1}(r_B) j_{\ell_2}(\kappa r_0) Y^m_{\ell_2}(r_0) z_0 \, d^3r$

We evaluate this kind of integrals by using the same coordinate system as defined in the treatment of I_{BB}, i.e., with 0 and B as the two foci. The result after some straight-forward algebra is:

$$I_{BO} = N_{\ell_1}^m N_{\ell_2}^m (-1)^{\ell_1} (\tfrac{1}{2}R_{BO})^4 (\kappa R_{BO})^{-3} \int_{\}'_0}^{\frac{2}{\}}+1} d\xi \sum_{u=0}^{m} \sum_{v=0}^{2u} \sum_{\nu_1=0}^{[\frac{1}{2}(\ell_1-m)]}$$

$$\sum_{\nu_2=0}^{[\frac{1}{2}(\ell_2-m)]} \sum_{r=0}^{\ell_1-m-2\nu_1} \sum_{s=0}^{\ell_2-m-2\nu_2} \{(-1)^{u+v+\ell_1-2\nu_1} \omega_{\nu_1}^{\ell_1 m} \omega_{\nu_2}^{\ell_2 m} C_u^m C_v^{2u}$$

$$\times C_r^{\ell_1-m-2\nu_1} 2(\kappa R_{BO})^{r+s-2u+v+2m} (1-\xi^2)^{m+r+s} \xi^{v+\ell_1-m-2\nu_1-r}$$

$$\times \xi^{\ell_2-m-2\nu_2-s} \{(1-\xi^2) h_{\ell_1\ell_2}^4 (s-2u+v+m, r+m, \xi) + (\xi/\kappa R_{BO})$$

$$\times h_{\ell_1\ell_2}^4 (s-2u+v+m-1, r+m, \xi)\}\}$$

where the h^4-functions are defined as:

$$h_{\ell_1\ell_2}^4 (r,s,\xi) = \sum_{u=0}^{1} \sum_{v=0}^{1} \sum_{k_1=0}^{[\frac{1}{2}(\ell_1-u)]} \sum_{k_2=0}^{[\frac{1}{2}(\ell_2-v)]} (-1)^{u+k_1+k_2} (\ell_1+\tfrac{1}{2}, 2k_1+u)$$

$$\times (\ell_2+\tfrac{1}{2}, 2k_2+v) Q_{\ell_1\ell_2}^{(u,v,4)} (r+2k_2+v, s+2k_1+u, \xi)$$

and the Q-functions are defined as:

$$Q_{\ell_1\ell_2}^{(u,v,4)} (p,q,\xi) = \{\sin(\kappa R_{BO}\xi - \tfrac{1}{2}(\ell_1+\ell_2)\pi)(\delta_{u+v,0} - \delta_{u+v,2})$$

$$+ \cos(\kappa R_{BO}\xi - \tfrac{1}{2}(\ell_1+\ell_2)\pi) \delta_{u+v,1}\}$$

$$\times \int_{\kappa R_{BO}(\}-\}_1(\}))}^{\kappa R_{BO}(\}-\}_2(\}))} \cos t / \{(2\kappa R_{BO}\xi - t)^p t^q\} dt$$

$$+ \{\cos(\kappa R_{BO}\xi - \tfrac{1}{2}(\ell_1+\ell_2)\pi) (\delta_{u+v,2} - \delta_{u+v,0})$$

$$+ \sin(\kappa R_{B0}\xi - \tfrac{1}{2}(\ell_1 + \ell_2)\pi) \; \delta_{u+v,1}\}$$

$$\times \int_{\kappa R_{B0}(\zeta - \vartheta_1(\zeta))}^{\kappa R_{B0}(\zeta - \vartheta_2(\zeta))} \sin t / \{(2\kappa R_{B0}\xi - t)^p t^q\} \; dt$$

$$+ \{\sin(\kappa R_{B0}\xi + \tfrac{1}{2}(\ell_1 - \ell_2)\pi) \; (\delta_{u+v,0} + \delta_{u+v,2})$$

$$+ \cos(\kappa R_{B0}\xi + \tfrac{1}{2}(\ell_1 - \ell_2)\pi) \; \delta_{u+v,1}(\delta_{u,0} - \delta_{u1})\}$$

$$\times \int_{\kappa R_{B0}(\zeta - \vartheta_1(\zeta))}^{\kappa R_{B0}(\zeta - \vartheta_2(\zeta))} 1 / \{(2\kappa R_{B0}\xi - t)^p t^q\} \; dt$$

(5) I_{00}: $\int_{II} j_{\ell_1}(\kappa r_0) Y_{\ell_1}^m(\vec{r}_0) j_{\ell_2}(\kappa r_0) Y_{\ell_2}^m(\vec{r}_0) z_0 \; d^3r$

Since $\quad Y_{\ell_1}^m(\vec{r}_0) Y_{\ell_2}^m(\vec{r}_0) = \sum_{\ell_3, m_3} I(\ell_1, m; \ell_2, m; \ell_3, m_3) Y_{\ell_3}^{m_3}(\vec{r}_0)$

therefore $\quad I_{00} = \sum_{\ell_3, m_3} I(\ell_1, m; \ell_2, m; \ell_3, m_3)$

$$\times \int_{II} j_{\ell_1}(\kappa r_0) j_{\ell_2}(\kappa r_0) Y_{\ell_3}^{m_3}(\vec{r}_0) z_0 \; d^3r$$

Since the integrand depends on ϕ only through $Y_{\ell_3}^{m_3}(\vec{r}_0)$, therefore, after integrating over ϕ, the only nonvanishing term is the one with $m_3 = 0$. Thus, we have:

$$I_{00} = \sum_{\ell_3 = |\ell_1 - \ell_2|}^{\ell_1 + \ell_2} I(\ell_1, m; \ell_2, m; \ell_3, 0) \int_{II} j_{\ell_1}(\kappa r_0) j_{\ell_2}(\kappa r_0) Y_{\ell_3}^0(\vec{r}_0) z_0 \; d^3r$$

Also, since $Y_{\ell_3}^0(\vec{r}_0) z_0 = Y_{\ell_3}^0(\vec{r}_0) r_0 \cos\theta_0$

$$= (4\pi/3)^{\tfrac{1}{2}} r_0 Y_{\ell_3}^0(\vec{r}_0) \; Y^0(\vec{r}_0)$$

$$= (4\pi/3)^{\frac{1}{2}} r_0 \sum_{\ell_4 = |\ell_3 - 1|}^{\ell_3 + 1} I(\ell_3, 0; 1, 0; \ell_4, 0) Y^0_{\ell_4}(\vec{r}_0)$$

therefore $\quad I_{00} = (4\pi/3)^{\frac{1}{2}} \sum_{\ell_3 = |\ell_1 - \ell_2|}^{\ell_1 + \ell_2} \sum_{\ell_4 = |\ell_3 - 1|}^{\ell_3 + 1} I(\ell_1, m; \ell_2, m; \ell_3, 0)$

$$\times I(\ell_3, 0; 1, 0; \ell_4, 0) \int_{II} j_{\ell_1}(\kappa r_0) j_{\ell_2}(\kappa r_0) Y^0_{\ell_4}(\vec{r}_0)$$

$$\times r_0 \, d^3 r$$

Employing the Prolate Spheroidal Coordinates as in the evaluation of I_{B0}, and expanding the integrand in terms of these coordinates, we have:

$$\int_{II} j_{\ell_1}(\kappa r_0) j_{\ell_2}(\kappa r_0) r_0 Y^0_{\ell_4}(\vec{r}_0) \, d^3 r$$

$$= N^0_{\ell_4} (2\pi)^{\frac{1}{2}} (R_{B0}/2)^4 (\kappa R_{B0})^{-3} \sum_{\nu=0}^{[\frac{1}{2}\ell_4]} \omega^{\ell_4 0}_{\nu} \sum_{r=0}^{\ell_4 - 2\nu} (\kappa R_{B0})^r$$

$$\int_{\}'_0}^{\frac{1}{r}+1} d\xi \, \{\xi^{\ell_4 - 2\nu - r} (1-\xi^2)^r \, \{2\xi \int_{\kappa R_{B0}(\} + \jmath_1(\})}^{\kappa R_{B0}(\} + \jmath_2(\})} j_{\ell_1}(\tfrac{1}{2}t) j_{\ell_2}(\tfrac{1}{2}t)/t^{r-2} \, dt$$

$$- (1/\kappa R_{B0}) \int_{\kappa R_{B0}(\} + \jmath_1(\})}^{\kappa R_{B0}(\} + \jmath_2(\})} j_{\ell_1}(\tfrac{1}{2}t) j_{\ell_2}(\tfrac{1}{2}t)/t^{r-3} \, dt\}\}$$

(6) I_{AB}: $\displaystyle\int_{II} \eta_{\ell_1}(\kappa r_A) Y^m_{\ell_1}(\vec{r}_A) \eta_{\ell_2}(\kappa r_B) Y^m_{\ell_2}(\vec{r}_B) z_0 \, d^3 r$

This is a three-center integral. But we can write z_0 as $z_A - R_{A0}$ and reduce it to a two-center integral. We shall evaluate this integral by using the Prolate Spheroidal Coordinates, in this case, with A and B as the two foci:

$$\xi = (r_A + r_B)/R \; ; \qquad \eta = (r_A - r_B)/R \; ; \qquad \phi = \phi_A = \phi_B$$

With this coordinate system, we have the following restrictions for the transformed intersphere region:

(i) $r_A \geqslant R_A$ or $\xi + \eta \geqslant 2(1 - \beta)$

(ii) $r_B \geqslant R_B$ or $\xi - \eta \geqslant 2\beta$

(iii) $r_0 \leqslant R$

Since $r_0^2 = r_A^2 + R_{A0}^2 - 2r_A R_{A0} \cos\Theta_A \leqslant R^2$

Therefore $\xi^2 - (4\beta-2)\xi\eta + \eta^2 - (4+4\beta-4\beta^2) \leqslant 0$

(iv) $\xi \geqslant 1$

(v) $-1 \leqslant \eta \leqslant 1$

Combining the above five restrictions, we have the transformed region as defined by the following limits (figure (5.4)):

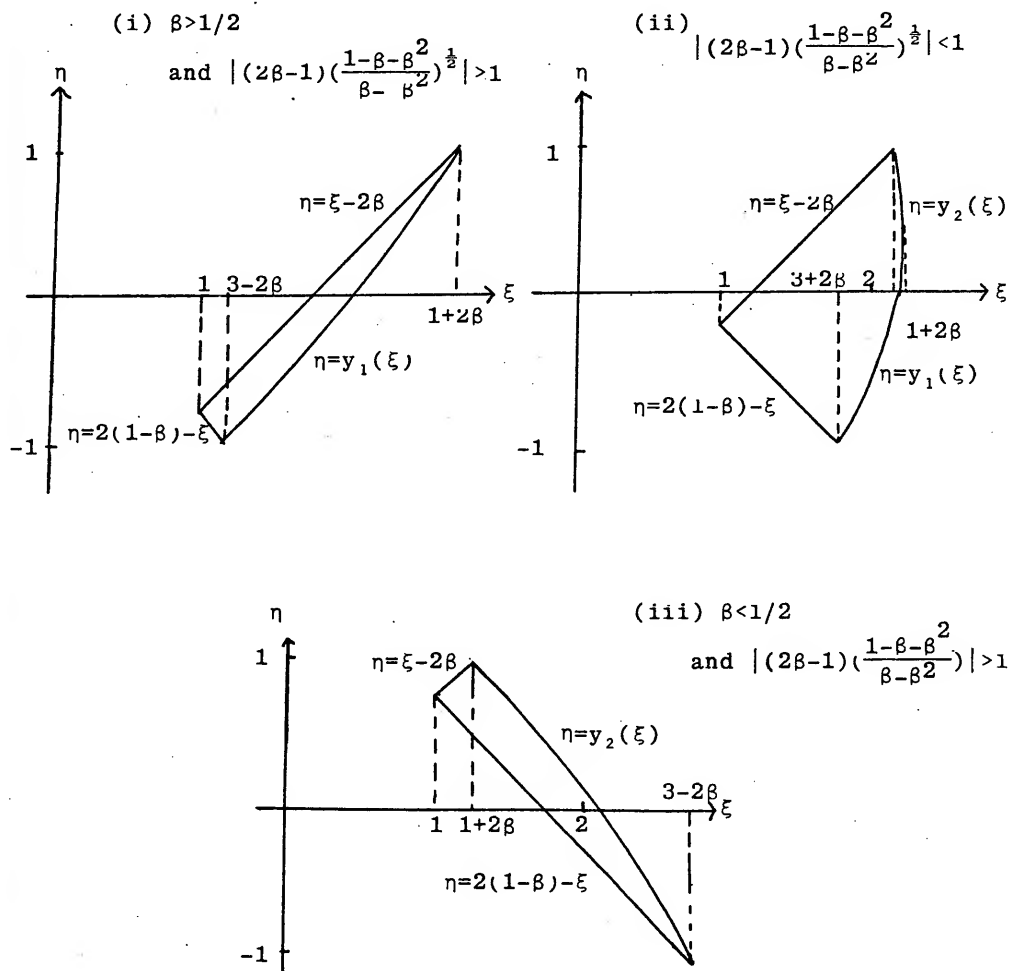$$1 \leqslant \xi \leqslant \xi_{max} \; ; \qquad y_1(\xi) \leqslant \eta \leqslant y_2(\xi)$$

Fig. 5.4 Boundary of the Intersphere Region in Prolate
Spheroidal Coordinates with A and B as the Foci.

where

$$\xi_{max} = \begin{cases} \{(1+\beta-\beta^2)/(\beta-\beta^2)\}^{\frac{1}{2}} & \text{if } |(2\beta-1)\{(1-\beta-\beta^2)/(\beta-\beta^2)\}^{\frac{1}{2}} < 1 \\[3mm] 1 + 2\beta & \text{if } \beta > \frac{1}{2} \text{ and } (2\beta-1)\{(1-\beta-\beta^2)/(\beta-\beta^2)\}^{\frac{1}{2}} > 1 \\[3mm] 3 - 2\beta & \text{otherwise} \end{cases}$$

$$y_1(\xi) = \begin{cases} 2(1-\beta)-\xi & \text{if } \xi \leqslant 3-2\beta \\[3mm] (2\beta-1)\xi-2\{1-(\beta-\beta^2)(\xi^2-1)\}^{\frac{1}{2}} & \text{otherwise} \end{cases}$$

$$y_2(\xi) = \begin{cases} \xi-2\beta & \text{if } \xi \leqslant 2\beta+1 \\[3mm] (2\beta-1)\xi+2\{1-(\beta-\beta^2)(\xi^2-1)\}^{\frac{1}{2}} & \text{otherwise} \end{cases}$$

Expanding the spherical harmonics and the Neumann functions in terms of ξ, η and ϕ, we have:

$$I_{AB} = N_{\ell_1}^m\, N_{\ell_2}^m\, (-1)^{\ell_1+\ell_2}\, (R/2)^3 (\ R)^{-3} \int_1^{\xi_{max}} d\xi \sum_{u=0}^m \sum_{v=0}^{2u} \sum_{\nu_1=0}^{[\pm(\ell_1-m)]}$$

$$\sum_{r=0}^{\ell_1-m-2\nu_1} \sum_{\nu_2=0}^{[\pm(\ell_2-m)]} \sum_{s=0}^{\ell_2-m-2\nu_2} \{(-1)^{u+v+\ell_2-2\nu_2}\ \omega_{\nu_1}^{\ell_1 m}\ \omega_{\nu_2}^{\ell_2 m}$$

$$\times\ C_u^m\, C_v^{2u}\, C_r^{\ell_1-m-2\nu_1}\, C_s^{\ell_2-m-2\nu_2}\, 2(\kappa R)^{\ell_1-2\nu_1-2u+v-r+\ell_2-2\nu_2-s}$$

$$\times\ \xi^{v+r+s}\, (1-\xi^2)^{\ell_1-m-2\nu_1-r+\ell_2-2\nu_2-s}\ \{\ (R/2-R_{A0}-\xi^2 R/2)$$

$$\times\ h_{\ell_1\ell_2}^5(\ell_1-2\nu_1-2u+v-r,\ \ell_2-2\nu_2-s,\ \xi)$$

$$+ \xi/(2\kappa)\ h^5_{\ell_1\ell_2}(\ell_1-2\nu_1-2u+v-r-1,\ell_2-2\nu_2-s,\xi)\}\}$$

where the h^5-functions are defined as:

$$h^5_{\ell_1\ell_2}(r,s,\xi) = \sum_{u=0}^{1}\sum_{v=0}^{1}\sum_{k_1=0}^{[\frac{1}{2}(\ell_1-u)]}\sum_{k_2=0}^{[\frac{1}{2}(\ell_2-v)]}(-1)^{u+v+k_1+k_2}(\ell_1+\tfrac{1}{2},2k_1+u)$$

$$\times\ (\ell_2+\tfrac{1}{2},2k_2+v)Q^{(u,v,5)}_{\ell_1\ell_2}(r+2k_1+u,s+2k_2+v,\xi)$$

and the Q-functions are defined as:

$$Q^{(u,v,5)}_{\ell_1\ell_2}(p,q,\xi) = \{\ \cos(\kappa R\xi-\tfrac{1}{2}(\ell_1-\ell_2)\pi)\ (\delta_{u+v,0}+\delta_{u+v,2})$$

$$+\ \sin\ (\kappa R\xi-\tfrac{1}{2}(\ell_1-\ell_2)\pi)\ \delta_{u+v,1}(\delta_{u,0}-\delta_{u,1})\}$$

$$\times\ \int_{\kappa R(\zeta+\gamma_1(\zeta))}^{\kappa R(\zeta+\gamma_2(\zeta))}\cos t/\{t^p(2\kappa R\xi-t)^q\}dt$$

$$+\{\sin(\kappa R\xi-\tfrac{1}{2}(\ell_1-\ell_2)\pi)\ (\delta_{u+v,0}+\delta_{u+v,2})$$

$$+\ \cos(\kappa R\xi-\tfrac{1}{2}(\ell_1-\ell_2)\pi)\ \delta_{u+v,1}(\delta_{u1}-\delta_{u0})$$

$$\times\ \int_{\kappa R(\zeta+\gamma_1(\zeta))}^{\kappa R(\zeta+\gamma_2(\zeta))}\sin t/\{t^p(2\kappa R\xi-t)^q\}dt$$

$$+\ \{\cos(\kappa R\xi+\tfrac{1}{2}(\ell_1+\ell_2)\pi)\ (\delta_{u+v,0}-\delta_{u+v,2})$$

$$+\ \sin(\kappa R\xi+\tfrac{1}{2}(\ell_1+\ell_2)\pi)\ \delta_{u+v,1}\}$$

$$\times\ \int_{\kappa R(\zeta+\gamma_1(\zeta))}^{\kappa R(\zeta+\gamma_2(\zeta))}1/\{t^p(2\kappa R\xi-t)^q\}dt$$

To conclude this section, we note that, as we did in the force calculations, we have reduced all the integrals into a sum of one-dimensional integrals which involve the sine and cosine integrals. We shall discuss the evaluation of these integrals in Appendix G. Also, we note that the actual calculation is not as awkward as the equations might suggest. Since the ℓ-values used as basis functions are always small, we have only very few terms in all the summations, as we noted in the force calculations.

5.3 Results and Discussion

The dipole moment calculations have been carried out for several diatomic molecules: lithium hydride, boron hydride and carbon hydride. Lithium hydride is investigated because it is the simplest heteronuclear diatomic molecule, boron hydride because it is more complicated but still only. involves σ orbitals in its ground state and is of closed-shell configuration, and carbon hydride because it also involves a π orbital. Also, there are experimental values or some other theoretical results of the dipole moments for these molecules with which we can compare to our results.

Lithium Hydride LiH:

The ground state of LiH is $^1\Sigma^+$, and the electronic configuration is $1\sigma^2 2\sigma^2$. The states 1σ are formed from the two 1s orbitals of the lithium atom while the two outer electrons occupying 2σ orbitals form the bonding. Thus, the ground state is ionic (Li^+H^-).

(1) In order to obtain a dipole moment curve with the dipole moment against the bond distance. Four non-spin-polarized MSXα calculations have been carried out for four different separations: R=2.75 a.u., 2.836 a.u., 3.015 a.u. and 3.25 a.u. Each of the calculations is done with the optimized β value ($\beta=R_{Li}/R$) which had obtained by Linsen-meyer (see Linsenmeyer (1974)), so that the muffin-tin total energy obtains the minimum at each of the four separations: β =1.34/2.75 at R=2.75 a.u., β=1.39/2.836 at R=2.836 a.u., β=1.49/3.015 at R=3.015 a.u., and β=1.63/3.25 at R=3.25 a.u. Also, the spin-polarized α values are used: α_{Li}=0.77159, α_H=0.77627, $\alpha_{II}=\alpha_{out}=(\alpha_{Li}+\alpha_H)/2$, and the ℓ values are used up to 3 in the lithium atomic sphere and the outer sphere while ℓ=0,1 in the hydrogen atomic sphere. The results of the dipole moment values calculated by using the converged MSXα wavefunctions are listed in table (5.1). The dipole moments are plotted against R in figure (5.5).

The value of the dipole moment at the experimental equilibrium separation R=3.015 a.u. is $\mu_{x\alpha}(\tilde{\rho})$= 7.289 Debyes. Compared with the experimental value μ_{exp}=5.879 Debyes or with the configuration interaction result obtained by Bender and Davidson (see Bender and Davidson (1968)): μ_{CI}=6.04 Debyes, our result is about 24% larger. However, if we look at the value obtained by assuming the muffin-tin charge density with equation (3.6): $\mu_{x\alpha}(\bar{\rho})$=3.332 Debyes which is about 44% less than the experimental value, we see that our result is defi-nitely an improvement.

TABLE 5.1

Dipole Moment Components for LiH ($^1\Sigma^+$)
at R=2.75, 2.836, 3.015, 3.25 a.u.

	R=2.75	R=2.836	R=3.015	R=3.25
$\mu_H^{1\sigma}$	-0.000660	-0.000547	-0.000370	-0.000217
$\mu_{Li}^{1\sigma}$	1.35972	1.40261	1.49290	1.59927
$\mu_{out}^{1\sigma}$	0.013375	0.011243	0.007885	0.004774
$\mu_{II}^{1\sigma}$	0.	0.	0.	0.
$\mu_H^{2\sigma}$	-0.540407	-0.573004	-0.642463	-0.737138
$\mu_{Li}^{2\sigma}$	0.020414	0.020601	0.21286	0.022991
$\mu_{out}^{2\sigma}$	-0.526761	-0.518479	-0.500600	-0.480344
$\mu_{II}^{2\sigma}$	-0.22059	-0.23700	-0.27030	-0.32862
$\mu_e^{1\sigma}$	1.37244	1.41331	1.50041	1.60383
$\mu_e^{2\sigma}$	-1.26734	-1.30788	-1.39208	-1.52311
μ_e^{total}	0.21020	0.21086	0.21666	0.16143
μ_N	2.890	2.948	3.085	3.230
$\mu_{x\alpha}(\tilde\rho)$	2.680	2.737	2.868	3.069

* R in a.u.
  μ in e-a_0.
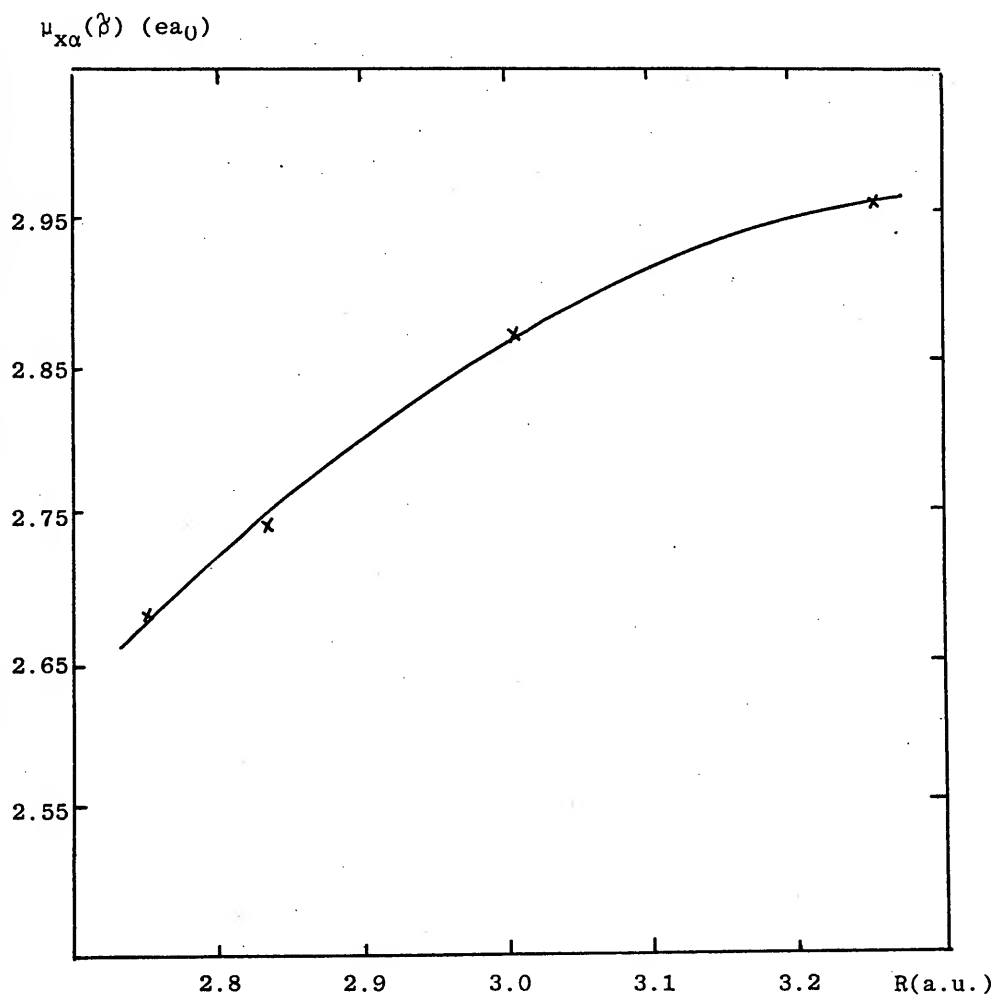
Fig. 5.5 Dipole Moment v.s. Seperation for LiH ($^1\Sigma^+$)

TABLE 5.2

Dipole Moments and Their Derivatives for LiH at R=3.015 a.u.

	μ (D)	$\frac{\partial \mu}{\partial R}$ (D/a.u.)
C.I.	6.04	1.225^{a}, 1.31^{b}
Exp't	5.88	1.068
M-T Density	3.33	2.38
Our Method	7.29	1.27

[a] See Yde and others (1972)
[b] See Ebbing (1962)

TABLE 5.3

β and ℓ- Dependence of Dipole Moment for LiH at R=3.015 a.u.

	#1	#2	#3
$\mu_H^{1\sigma}$	-0.000370	-0.000399	-0.000370
$\mu_{Li}^{1\sigma}$	1.49290	1.53599	1.49291
$\mu_{out}^{1\sigma}$	0.007885	0.009144	0.007885
$\mu_{II}^{1\sigma}$	0.	0.	0.
$\mu_H^{2\sigma}$	-0.642463	-0.643122	-0.643129
$\mu_{Li}^{2\sigma}$	0.021286	0.020384	0.021401
$\mu_{out}^{2\sigma}$	-0.500600	-0.486677	-0.494427
$\mu_{II}^{2\sigma}$	-0.27030	-0.20944	-0.25163
$\mu_e^{1\sigma}$	1.50041	1.54474	1.50042
$\mu_e^{2\sigma}$	-1.39208	-1.31885	-1.36778
μ_e^{total}	0.21666	0.45177	0.26528
μ_N	3.085	3.285	3.085
$\mu_{x\alpha}(\tilde{\rho})$	2.868	2.833	2.820

#1: β=1.49/3.015, ℓ=0,1,2,3 in both the Li and the outer
    sphere, ℓ=0,1 in the H sphere.
#2: β=1.44/3.015, ℓ=0,1,2,3 in both the Li and the outer
    sphere, ℓ=0,1 in the H sphere.
#3: β=1.49/3.015, ℓ=0,1,2 in both the Li and the outer
    sphere, ℓ=0,1 in the H sphere.
μ in unit of e-a_0

Also, the value of the derivative of the dipole moment at the experimental separation is equal to 1.27 Debyes/a.u. Compared with the experimental value 1.068 Debyes/a.u. and two other values by Yde(1972) and Ebbing (1962) (1.225 Debyes/a.u. and 1.31 Debyes/a.u.), our result is very satisfactory. Furthermore, we again note that it is an improvement over the value (2.38 Debyes/a.u.) which is about two times the correct value. The different results are listed in table (5.2).

(2) In order to check the sensitivity of the value of the dipole moment to the way of partitioning the coordinate space, we repeat the calculation at R=3.015 a.u. but with a different value of β ($\beta=1.44/3.015=0.477$). The results are listed in colume 2 of table (5.3). The result of the dipole moment for this β is 2.833 ea_0. Comparing it with the value obtained with the optimized β value ($\beta_{opt}=0.499$), 2.868 ea_0, we see the value of the dipole moment is not very sensitive to the change of β, at least for this molecule.

(3) In order to check the sensitivity of the value of the dipole moment to the number of basis functions used, we repeat the calculation at R = 3.015 a.u. but with a different set of bases: $\ell = 0,1,2$ in the lithium sphere and the outer sphere; $\ell = 0,1$ in the hydrogen sphere. In both cases we use $\beta = 1.49/3.015$. The results are listed in column 3 of table (5.3). Comparing this result $\mu=2.820$ ea_0 with the previous result $\mu=2.868$ ea_0, we see that the value

of the dipole moment is quite sensitive to the basis func-
tions used.

Boron Hydride BH:

The ground state for BH is $^1\Sigma^+$ and the electronic
configuration is $1\sigma^2 2\sigma^2 3\sigma^2$. The MSX$\alpha$ calculation is carried
out for this molecule at the experimental equilibrium sep-
aration R_e=2.336 a.u. The ratio of the radii of the spheres
is chosen to be $\beta=R_B/R=1.59/2.336$ that optimizes the muffin-
tin total energy at R_e. Also, we use the spin-polarized α
values: α_B=0.76206, α_H=0.77627, $\alpha_{II}=\alpha_{out}=(\alpha_B+\alpha_H)/2$. The ℓ-
values used are up to 3. The results for the dipole moment
calculation are listed in table (5.4).

The result obtained is $\mu_{x\alpha}(\tilde{\rho})$=-1.24 Debyes. The exper-
imental value for the molecule is not available. However,
comparing it with the result calculated by Bender and David-
son using natural orbital configuration interaction method:
μ=-1.47 Debyes, we have quite a good agreement. Also, the
dipole moment calculated with the muffin-tin charge density
as suggested in Chapter III is $\mu_{x\alpha}(\bar{\rho})$=+1.15 Debyes which is
far away from both of the two results obtained above.

Carbon Hydride CH:

The ground state for CH is $^2\Pi$ at the equilibrium
separation R_e=2.124 a.u. and the electronic configuration
is $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^1$. The MSX$\alpha$ result is obtained with the follow-
ing parameters:

$\beta = R_e/R = 1.543/2.124$ which optimizes the muffin-
tin total energy,

TABLE 5.4

Dipole Moment for BH ($^1\Sigma^+$) at R=2.336 a.u.

	$1\sigma^2$	$2\sigma^2$	$3\sigma^2$
μ_H^i	-0.0000015	-0.134301	-0.086499
μ_B^i	0.745994	0.084568	0.417390
μ_{out}^i	0.0000345	-0.148342	0.664901
μ_{II}^i	0.	-0.228517	-0.000995
μ_e^i	0.746023	-0.42659	0.994996

μ_e^{total} = 2.628858 e-a_0

μ_N = 2.140 e-a_0

$\mu_{x\alpha}(\tilde{\rho})$ = -0.489 e-a_0 = -1.24 D

$\mu_{C.I.}^a$ = -1.47 D

$\mu_{x\alpha}(\overline{\rho})$ = +1.15 D

[a] See Bender and Davidson (1969)

TABLE 5.5

Dipole Moment for CH ($^2\Pi$) at R=2.124 a.u.

	$1\sigma^2$	$2\sigma^2$	$3\sigma^2$	$1\pi^1$
μ_H^i	-0.00000014	-0.042175	-0.062419	-0.000543
μ_C^i	0.581002	0.174046	0.397942	0.259628
μ_{out}^i	0.00000380	0.025876	0.288481	0.171516
μ_{II}^i	0.	-0.115285	-0.089127	-0.033806
μ_e^i	0.581005	0.042463	0.534878	0.396796

μ_e = 2.713488 e-a_0

μ_N = 1.943 e-a_0

$\mu_{x\alpha}(\tilde{\rho})$ = -0.7705 e-a_0 = -1.958 D

$\mu_{C.I.}^a$ = -1.472 D

$\mu_{x\alpha}(\bar{\rho})$ = -0.04 D

$\mu_{exp't}$ = -1.46 $\pm$ 0.06 D

[a] See Bender and Davidson(1969).

$$\alpha_C = 0.75331; \quad \alpha_H = 0.77627; \quad \alpha_{II} = \alpha_{out} = 0.76479 \; ;$$

$$\ell_C = 0,1,2,3; \quad \ell_H = 0,1 \quad ; \quad \ell_{out} = 0,1,2,3 \quad ;$$

for the 1σ, 2σ, 3σ states

$$\ell_C = 1,2,3 \quad ; \quad \ell_H = 1,2 \quad ; \quad \ell_{out} = 1,2,3 \quad ;$$

for the 1π state.

The results of the dipole moment calculation are listed in table (5.5)

The result obtained is $\mu_{x\alpha}(\tilde{\rho}) = -1.958$ Debyes. Comparing it with the experimental value: $\mu_{exp} = -1.46 \pm 0.06$ Debyes, and also with the theoretical value obtained by Bender and Davidson using natural orbital configuration interaction, $\mu_{CI} = -1.472$ Debyes, we note the value that we got is not too different from these values. Indeed, it is a big improvement over the value obtained by using the muffin-tin charge density: $\mu_{x\alpha}(\vec{\rho}) = -0.04$ Debye.

CHAPTER VI

CONCLUSIONS

The main purpose of this dissertation was to investigate the quality of the MSXα wavefunctions. To achieve this, we performed the force and the dipole moment calculations by use of the charge density generated from the MSXα wavefunctions, instead of using the muffin-tin part of the density function.

With the results obtained for the dipole moment of LiH, BH and CH, we see that the use of the MSXα wavefunctions in such a dipole moment calculation is quite adequate even though it is well known that the dipole moment is very sensitive to the approximate wavefunctions used. The reason that we may expect, and we do have, adequate results for the calculation of the dipole moment with the MSXα wavefunctions is as follows. In the MSXα method, the constant potential and charge distribution in the intersphere region is the most severe approximation, and thus the MSXα wavefunction differs most from the exact Xα wavefunction in this region. However, the amount of the total charge in this region is much smaller than that in the other regions, and furthermore, if we take the center of the outer sphere as the origin of the whole system, we have quite a large cancellation of the errors in--volved in the contribution by the electronic charge cloud

110

in the intersphere region. Therefore, the net result of the
dipole moment calculation is quite good with such MSXα
wavefunctions.

In the treatment of the heteronuclear diatomic
molecules, the calculation is more complicated because here
we have an arbitrary choice of the parameters: the ratio of
the radii of the spheres, and the α values in the intersphere
region and in the outer sphere. Though we have not broadly
investigated their effects on the results, we feel that they
do effect the result, as we have noticed in the treatment of
LiH.

However, in the treatment of homonuclear diatomic
molecules, we do not have such a problem of the choice of the
α values and the β values. The two atomic spheres have to be
the same size and the α value has to be a constant over the
whole space. Thus, in the Hellmann-Feynman force calculations
for H_2 and N_2, there are not any adjustable parameters except
the α value. Since the Hellmann-Feynman Theorem is satisfied
by the exact Xα wavefunctions no matter what α value is used,
the only approximation that causes the electrostatic force
to differ from the quantity $-\frac{\partial <E_{X\alpha}>}{\partial X_p}$ is the muffin-tin approx-
imation, through which the MSXα wavefunctions $\tilde{u}_i$ are obtained.
From the results for H_2 (figure(4.4)), we notice that there
is such a difference between the two quantities $F_{X\alpha}(\tilde{\rho})$ and
$-\frac{\partial <E_{X\alpha}(\tilde{\rho})>}{\partial X_p}$. Thus, at least for the case of H_2, there is a
difference between the MSXα wavefunctions and the exact Xα
wavefunctions.

As stated, another purpose of this dissertation is to suggest a method for the evaluation of the complicated three-dimensional integrals over the intersphere region. Actually, this method of using the Prolate Spheroidal Coordinates should not be limited to the force and dipole moment calculations. It can be employed in the evaluation of molecular properties that can be represented by some one-electron operators. Thus, for example, the transition amplitudes $<\tilde{u}_i|\vec{r}|\tilde{u}_j>$ between any two molecular states should be able to be evaluated by this method. Of course, the result would depend on whether the MSXα wavefunctions are accurate enough for the evaluation of such a sensitive quantity. The merit of this method of calculation is that all the integrals are reduced into some one dimensional integrals that can be handled in an efficient way.

Although in this dissertation we have only treated diatomic molecules, we can also apply our method to more complicated systems. To illustrate this, we give a brief discussion on the calculation of a quantity F for a triatomic molecule ABC.

As before, we partition the space into the outer region, the intersphere region and the atomic region(in this case, it includes the three spheres A, B, C)(figure(6.1)). The difficult part of the calculation is in the evaluation of the following integrals over the intersphere region II:
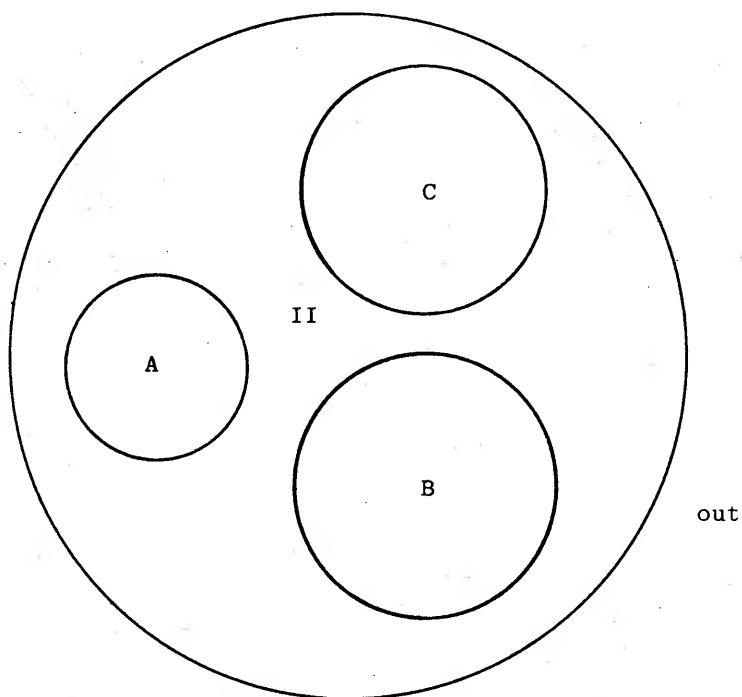
$$F^i = \int_{II} u_i^2(r)F(r)d^3r$$

Fig. 6.1 Schematic Representation of a Triatomic
Molecule in the MSXα Method

where $\tilde{u}_i(\vec{r})$ is the converged MSXα wavefunction for the ith molecular state.

As before, the evaluation of F^i can be reduced to the evaluations of integrals like:

$$F^i_{AB} = \int_{II} \eta_{\ell_1}(\kappa r_A)Y^{m_1}_{\ell_1}(\vec{r}_A)\eta_{\ell_2}(\kappa r_B)Y^{m_2}_{\ell_2}(\vec{r}_B)F(\vec{r})d^3r \qquad (6.1)$$

We can evaluate F^i_{AB} by changing the region of integration to the intersphere region plus the sphere C, and then substract from it the contribution from the atomic sphere C:

$$F^i_{AB} = \int_{II+C} \eta_{\ell_1}(\kappa r_A)Y^{m_1}_{\ell_1}(\vec{r}_A)\eta_{\ell_2}(\kappa r_B)Y^{m_2}_{\ell_2}(\vec{r}_B)F(\vec{r})d\,r$$

$$- \int_C \eta_{\ell_1}(\kappa r_A)Y^{m_1}_{\ell_1}(\vec{r}_A)\eta_{\ell_2}(\kappa r_B)Y^{m_2}_{\ell_2}(\vec{r}_B)F(\vec{r})d^3r \qquad (6.2)$$

To evaluate the first term, we note that since the integrand has poles only at centers A and B, and both of them are excluded from the region of integration, there is no problem of divergence. So this term looks like the previous integrals that we encountered in the diatomic case, and we want to apply our method to the evaluation of this term. However, generally the spherical harmonics $Y^m_\ell(\vec{r}_A)$ and $Y^m_\ell(\vec{r}_B)$ are not defined relative to the internuclear axis R_{AB} as they are in the case of a diatomic molecule. Thus we first rotate the coordinates of both A and B in such a way that the new z-axes of both atoms are oriented along the internuclear
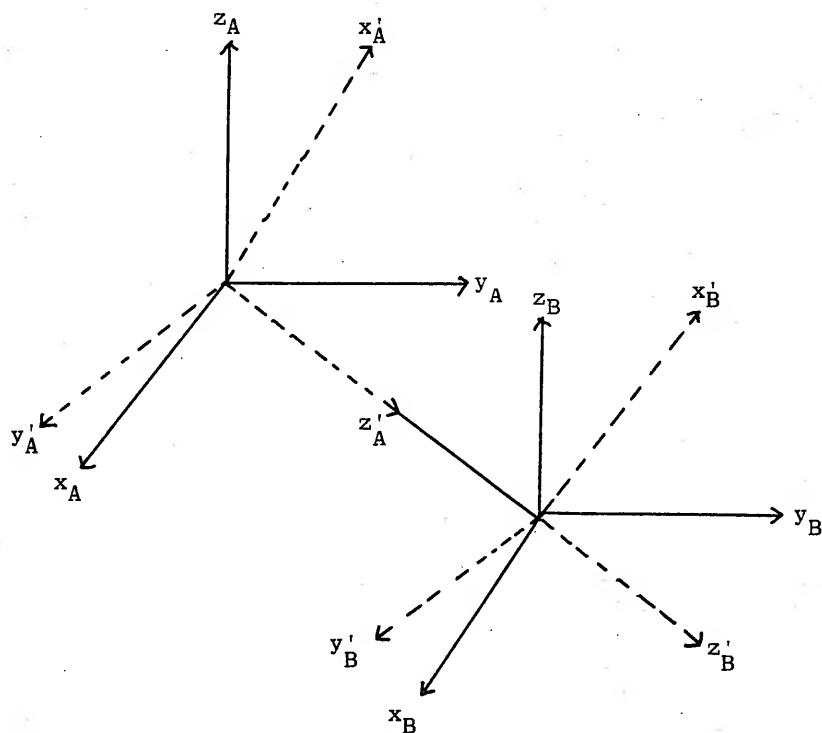
Fig. 6.2 Rotation of Atomic Coordinates to Align with the Internuclear Axis.

axis R_{AB} and both the x-axes and y-axes be coplanar with R_{AB} (figure(6.2)).With this rotation, the complex spherical harmonics are transformed as:

$$\mathcal{y}_{\ell}^{m}(\theta_A,\phi_A) = \sum_{m'=-\ell}^{\ell} \mathcal{y}_{\ell}^{m'}(\theta_A',\phi_A') \, D_{mm'}^{\ell}(\alpha_A,\beta_A,\gamma_A)$$

where $D_{mm'}^{\ell}$ are the rotational matrix elements and α_A, β_A, γ_A are the Euler angles of the new coordinates with respect to the old coordinates centered at A. Since the real spherical harmonics Y_{ℓ}^{m} can be written as:

$$Y_{\ell}^{m} = (\mathcal{y}_{\ell}^{m} + (-1)^{m}\mathcal{y}_{\ell}^{-m})/2^{\frac{1}{2}} \qquad \text{for } m > 0$$

the transformed real spherical harmonics are:

$$Y_{\ell}^{m}(\theta_A,\phi_A) = \sum_{m'=-\ell}^{\ell} \mathcal{y}_{\ell}^{m'}(\theta_A',\phi_A') \, \mathcal{D}_{mm'}^{\ell}(\omega_{A,AB}) \qquad (6.3)$$

where $\mathcal{D}_{mm'}^{\ell}(\omega_{A,AB}) = D_{mm'}^{\ell}(\alpha_A,\beta_A,\gamma_A) + (-1)^{m}D_{\overline{m}m'}^{\ell}(\alpha_A,\beta_A,\gamma_A)$ and similarly for $Y_{\ell}^{m}(\theta_B,\phi_B)$. Quite similarly is for $m \leq 0$. Thus the first term in equation (6.2) is equal to:

$$\sum_{m'=-\ell_1}^{\ell_1} \sum_{m'=-\ell_2}^{\ell_2} \mathcal{D}_{m_1 m_1'}^{\ell}(\omega_{A,AB}) \, \mathcal{D}_{m_2 m_2'}^{\ell}(\omega_{B,AB})$$

$$\times \int_{II+C} \eta_{\ell_1}(\kappa r_A)\mathcal{y}_{\ell_1}^{m_1'}(\vec{r}_A')\eta_{\ell_2}(\kappa r_B)\mathcal{y}_{\ell_2}^{m_2'}(\vec{r}_B')F(\vec{r})d^3r'$$

and now we can apply our method to the evaluation of these two-center integrals. Before that, we have to expand $F(\vec{r})$

about A:

$$F(\vec{r}) = \sum_{\ell_3 = 0}^{\infty} \sum_{m_3 = -\ell_3}^{\ell_3} F_{\ell_3}^{m_3}(r') \mathcal{Y}_{\ell_3}^{m_3}(\vec{r}')$$

Then, we wind up with the evaluation of the integrals:

$$\mathcal{J} = \int_{II+C} \eta_{\ell_1}(\kappa r_A) \mathcal{Y}_{\ell_1}^{m_1'}(\vec{r}_A') \eta_{\ell_2}(\kappa r_B) \mathcal{Y}_{\ell_2}^{m_2'}(\vec{r}_B) F_{\ell_3}(r_A) \mathcal{Y}_{\ell_3}^{m}(\vec{r}_A') d^3 r'$$

By use of the Prolate Spheroidal Coordinates with the foci at A and B, we can reduce the integral into a two-dimensional integral through the evaluation of the ϕ coordinate:

$$\mathcal{J} = 2\pi \, \delta_{m_1' + m_2' + m_3, 0} \int_{II+C} \eta_{\ell_1}(\kappa r_A) P_{\ell_1}^{m_1'}(\cos\theta_A') \eta_{\ell_2}(\kappa r_B) P_{\ell_2}^{m_2'}(\cos\theta_B')$$

$$\times \, F_{\ell_3}^{-m_1'-m_2'}(r_A) P_{\ell_3}^{-m_1'-m_2'}(\cos\theta_A') \, d^3 r/d\phi$$

Since

$$P_{\ell_1}^{m_1'}(\cos\theta_A') P_{\ell_2}^{m_2'}(\cos\theta_B') P_{\ell_3}^{-m_1'-m_2'}(\cos\theta_A')$$

$$= N_{\ell_1}^{m_1'} N_{\ell_2}^{m_2'} N_{\ell_3}^{-m_1'-m_2'} (\sin\theta_A')^{m_1'} (\sin\theta_B')^{m_2'} (\sin\theta_A')^{-m_1'-m_2'}$$

$$\times \sum_{\gamma_1 = C}^{[\frac{1}{2}(\ell_1 - m_1')]} \sum_{\nu_2 = 0}^{[\frac{1}{2}(\ell_2 - m_2')]} \sum_{\gamma_3 = 0}^{[\frac{1}{2}(\ell_3 + m_1' + m_2')]} \omega_{\nu_1}^{\ell_1 m_1'} \omega_{\nu_2}^{\ell_2 m_2'} \omega_{\nu_3}^{\ell_3, -m_1'-m_2'}$$

$$\times \, (\cos\theta_A')^{\ell_1 - m_1' - 2\nu_1 + \ell_3 + m_1' + m_2' - 2\nu_3} \, (\cos\theta_B')^{\ell_2 - m_2' - 2\nu_2}$$

and

$$(\sin\theta_A')^{m_1'} (\sin\theta_B')^{m_2'} (\sin\theta_A')^{-m_1'-m_2'}$$

$$= (\sin\theta')^{m_2'} (\sin\theta')^{-m_2'}$$

$$= \{(\xi^2-1)(1-\eta^2)\}^{\frac{1}{2}m'_2}/(\xi-\eta)^{m'_2} \times \{(\xi^2-1)(1-\eta^2)\}^{-\frac{1}{2}m'_2}/(\xi-\eta)^{m'_2}$$

$$= \{(\xi+\eta)/(\dot\xi+\eta)\}^{m'_2}$$

and similarly for the cosine factors. Thus, we can apply our method of integration as before, except that the limits of integration are more complicated.

For the second term in equation (6.2), we can expand $\eta_{\ell_1}(\kappa r_A)Y^{m_1}_{\ell_1}(\vec{r}_A)$ and $\eta_{\ell_2}(\kappa r_B)Y^{m_2}_{\ell_2}(\vec{r}_B)$ about center C. Since inside sphere C, we have $r_C < R_{AC}$ and $r_C < R_{BC}$, so the expansion is:

$$\eta_\ell(\kappa r_A)Y^m_\ell(\vec{r}_A) = 4\pi \sum_{\ell',m'} \sum_{\ell'',m''} i^{\ell'-\ell-\ell''} I(\ell'm';\ell m;\ell''m'')$$

$$\times \eta_{\ell''}(\kappa R_{AC})Y^{m''}_{\ell''}(\vec{R}_{AC})j_{\ell'}(\kappa r_C)Y^{m'}_{\ell'}(\vec{r}_C)$$

and similarly for $\eta_\ell(\kappa r_B)Y^m_\ell(\vec{r}_B)$. Also, we expand $F(\vec{r})$ about center C:

$$F(\vec{r}) = \sum_{\ell,m} F^m_\ell(r_C)Y^m_\ell(\vec{r}_C)$$

Then we have the integrals:

$$\int_C j_{\ell'}(\kappa r_C)Y^{m'}_{\ell'}(\vec{r}_C)j_{\ell'}(\kappa r_C)Y^{m'}_{\ell'}(\vec{r}_C)F_{\ell_3}(r_C)Y^m_{\ell_3}(\vec{r}_C)d^3r$$

$$= I(\ell'm';\ell'm';\ell_3 m_3)\int_0^{R_C} j_{\ell'}(\kappa r_C)j_{\ell'}(\kappa r_C)F_{\ell_3}(r_C)r^2_C \, dr_C$$

which involves only one-dimensional integtals.

The formalism given above is quite general for any function $F(\vec{r})$. In particular, for the dipole moment $F(\vec{r})=z$ (or x, y), and the expansion in spherical harmonics then has terms only up to $\ell=1$. Similarly for the Hellmann-Feynman force function $F(\vec{r})=\cos\theta/r^2$ which corresponds to the spherical harmonic term $\ell=1$.

In conclusion, the use of the charge density generated from the MSXα wavefunctions does improve the results of dipole moment and force calculations over the use of the muffin-tin charge density. From the results of these two kinds of calculations, we see that the MSXα wavefunctions are quite adequate in such molecular property calculations. Any further improvements should come from the correction to wavefunctions that is a solution to the muffin-tin approximate Xα one-electron Schrödinger equation (2.6). In fact, such an approach is being carried out by Connolly, Williams and others.

DERIVATION OF THE MUFFIN-TIN Xα ONE-ELECTRON EQUATIONS

In Section 2.3, we mentioned that the necessary and sufficient condition for the muffin-tin total energy $\overline{<E_{x\alpha}(\overline{\rho})>}$ be a minimum is that the spin-orbitals $\tilde{u}_i$ satisfy the muffin-tin one-electron equations (2.6). We are going to show it in this appendix.

Starting from the non-muffin total energy expression:

$$\overline{<E_{x\alpha}(\overline{\rho})>} = \sum_i n_i \int \tilde{u}_i^*(\vec{r}_1)(-\nabla_1)\tilde{u}_i(\vec{r}_1)d^3r_1 + U_{NN} + \overline{U}_T$$

where $\tilde{u}_i$ are the spin-orbitals,

U_{NN} is the nuclear-nuclear interaction energy,

and $\overline{U}_T$ is the sum of the nuclear-electron coulomb energy $\overline{U}_{ne}$, the electron-electron coulomb energy $\overline{U}_{ee}$ and the exchange-correlation energy $\overline{U}_{ex}$:

$$\overline{U}_T = \overline{U}_{ne} + \overline{U}_{ee} + \overline{U}_{ex}$$

$$= \int \overline{\rho}(\vec{r}_1)V_{ne}(\vec{r}_1)d^3r_1 + \frac{1}{2} \int \overline{\rho}(\vec{r}_1)V_c(\overline{\rho},\vec{r}_1)d^3r_1$$

$$+ C_\alpha \int \{\overline{\rho}_\uparrow(\vec{r}_1)^{4/3} + \overline{\rho}_\downarrow(\vec{r}_1)^{4/3}\}d^3r_1 \qquad (A.1)$$

where $V_{ne}(\vec{r}_1) = \sum_{p=1}^{N} (-2Z_p)/|\vec{r}_1 - \vec{R}_p|$

$$V_c(\overline{\rho}, \vec{r}_1) = \int 2\overline{\rho}(\vec{r}_2)/r_{12} \, d^3r_2 \qquad\qquad (A.2)$$

$$C_\alpha = -\frac{9}{2} \alpha \, (3/(4\pi))^{1/3}$$

It can be shown that for any two functions f and g, with the corresponding $\overline{f}$ and $\overline{g}$, we have the following identity:

$$\int \overline{f}(\vec{r})g(\vec{r}) \, d^3r = \int \overline{f}(\vec{r})\overline{g}(\vec{r}) \, d^3r$$

Hence, we have:

$$\overline{U}_{ne} = \int \overline{\rho}(\vec{r}_1)V_{ne}(\vec{r}_1)d^3r_1 = \int \overline{\rho}(\vec{r}_1)\overline{V}_{ne}(\vec{r}_1)d^3r_1 \qquad (A.3)$$

$$\overline{U}_{ee} = \frac{1}{2} \int \overline{\rho}(\vec{r}_1)V_c(\overline{\rho},\vec{r}_1)d^3r = \frac{1}{2} \int \overline{\rho}(\vec{r}_1)V_c(\overline{\rho},\vec{r}_1)d^3r_1 \quad (A.4)$$

Now, let us look at the variation of $\overline{\langle E_{x\alpha}(\overline{\rho})\rangle}$ with respect to $\tilde{u}_i$ which is of spin s (either up or down). By using the functional derivative notation (see Volterra (1930)), we have:

$$\delta \overline{\langle E_{x\alpha}(\overline{\rho})\rangle} = \int \frac{\delta}{\delta\tilde{u}_i^*(\vec{r})} \overline{\langle E_{x\alpha}(\overline{\rho})\rangle} \, \delta\tilde{u}_i^*(\vec{r}) \, d^3r + \text{(complex conj.)}$$

Here $\tilde{u}_i^*(\vec{r})$ is an arbitrary variation of the function $\tilde{u}_i^*(\vec{r})$ over its whole range of definition. There is no contribution from the nuclear-nuclear interaction term since it is not a functional of the spin-orbitals. As to the kinetic energy

part, we have:

$$\delta\overline{U}_{K.E.} = \int \frac{\delta}{\delta\tilde{u}_i^*(\vec{r})} \sum_j n_j \int \tilde{u}_j(\vec{r}_1)(-\nabla_1^2)\tilde{u}_j(\vec{r}_1)d^3r_1 \delta\tilde{u}_i^*(\vec{r})d^3r$$

$$+ \text{(complex conjugate)}$$

$$= \iint n_i \delta(\vec{r}-\vec{r}_1)(-\nabla_1^2)\tilde{u}_i(\vec{r}_1)\delta u_i^*(\vec{r}) \, d^3r_1 d^3r_2 + \text{(c.c)}$$

Integrating over $\vec{r}_1$, we have

$$\delta\overline{U}_{K.E.} = \int n_i \delta\tilde{u}_i^*(\vec{r})\{-\nabla^2\tilde{u}_i(\vec{r})\} \, d^3r + \text{(c.c.)} \qquad (A.5)$$

The variation of the term $\overline{U}_T$ is more complicated because it depends on the spin-orbitals only through the muffin-tin charge densities $\rho_\uparrow$ and $\rho_\downarrow$ and we have to use the chain rule of differention generalized to functional derivatives to find $\overline{U}_T$:

$$\delta\overline{U}_T = \int \frac{\delta\overline{U}_T}{\delta\tilde{u}_i(\vec{r})} \delta\tilde{u}_i^*(\vec{r}) \, d^3r + \text{(c.c.)}$$

$$= \sum_{s'} \int d^3r \, \delta\tilde{u}_i^*(\vec{r}) \int d^3r' \frac{\delta\overline{U}_T}{\delta\overline{\rho}_{s'}(\vec{r}')} \frac{\delta\overline{\rho}_{s'}(\vec{r}')}{\delta\tilde{u}_i^*(\vec{r})} + \text{(c.c.)}$$

$$\qquad (A.6)$$

where $s' = \uparrow, \downarrow$

Since

$$\overline{\rho}_{s'}(\vec{r}') = \begin{cases} \frac{1}{4\pi} \int \sum_{j,s_j=s'} n_j\tilde{u}_j^*(\vec{r}')\tilde{u}_j(\vec{r}')d\Omega' & \text{if } \vec{r}' \text{ in sphere } \beta \\[2ex] \frac{1}{V_{II}} \int_{II} \sum_{j,s_j=s'} n_j\tilde{u}_j^*(\vec{r}')\tilde{u}_j(\vec{r}')d^3r' & \text{if } \vec{r}' \text{ in region II} \end{cases}$$

Hence

$$\frac{\delta \bar{\rho}_{s'}(\vec{r}')}{\delta \hat{\widetilde{u}}_i^*(\vec{r})} = \begin{cases} \frac{1}{4\pi} n_i \{ \int \delta(\vec{r}-\vec{r}') \hat{\widetilde{u}}_i(\vec{r}')d\Omega' \} \delta_{s_i,s'} & \text{if } \vec{r}' \text{ in } \beta \\ \\ \frac{1}{V_{II}} n_i \{ \int_{II} \delta(\vec{r}-\vec{r}'') \hat{\widetilde{u}}_i(\vec{r}'')d^3r'' \} \delta_{s_i,s'} & \text{if } \vec{r}' \text{ in } II \end{cases} \tag{A.7}$$

Return to (A.6), let us consider the variation of the term $\bar{U}_{ne}$, which is included in $\bar{U}_T$, with respect to $\bar{\rho}_{s'}$. From equation (A.3), we have:

$$\frac{\delta \bar{U}_{ne}}{\delta \bar{\rho}_{s'}(\vec{r}')} = \frac{\delta}{\delta \bar{\rho}_{s'}(\vec{r}')} \int \bar{\rho}(\vec{r}_1) \bar{V}_{ne}(\vec{r}_1) d^3r_1$$

$$= \frac{\delta}{\delta \bar{\rho}_{s'}(\vec{r}')} \sum_s \int \bar{\rho}_s(\vec{r}_1) \bar{V}_{ne}(\vec{r}_1) d^3r_1$$

$$= \sum_s \int \frac{\delta \bar{\rho}_{s'}(\vec{r}_1)}{\delta \bar{\rho}_{s'}(\vec{r}')} \bar{V}_{ne}(\vec{r}_1) d^3r_1$$

$$= \sum_s \int \delta_{s's} \delta(\vec{r}_1-\vec{r}') \bar{V}_{ne}(\vec{r}_1) d^3r_1$$

$$= \bar{V}_{ne}(r') \tag{A.8}$$

Secondly, let us consider the variation of the electron-electron coulomb energy term $\bar{U}_{ee}$ with respect to the variation of $\bar{\rho}_{s'}$. From equations (A.1) and (A.2), we have:

$$\frac{\delta \bar{U}_{ee}}{\delta \bar{\rho}_{s'}(\vec{r}')} = \frac{\delta}{\delta \bar{\rho}_{s'}(\vec{r}')} \frac{1}{2} \int \bar{\rho}(\vec{r}_1) V_c(\bar{\rho}, \vec{r}_1) d^3r_1$$

$$= \frac{\delta}{\delta \bar{\rho}_{s'}(\vec{r}')} \frac{1}{2} \sum_s \sum_{s''} \iint 2\rho_s(\vec{r}_1)\rho_{s''}(\vec{r}_2)/r_{12} \, d^3r_1 d^3r_2$$

$$= \sum_s \sum_{s''} \int d^3r_1 \bar{\rho}_s(\vec{r}_1) \int d^3r_2 \frac{1}{2r_{12}} \frac{\bar{\rho}_{s''}(\vec{r}_2)}{\bar{\rho}_{s'}(\vec{r}')}$$

$$+ \sum_{s} \sum_{s''} \int d^3r_2 \, \bar{\rho}_{s''}(\vec{r}_2) \int d^3r_1 \frac{1}{r_{12}} \frac{\delta \bar{\rho}_s(\vec{r}_1)}{\delta \bar{\rho}_{s'}(\vec{r}')}$$

$$= \sum_{s} \sum_{s''} \iint d^3r_1 \bar{\rho}_s(\vec{r}_1) \int d^3r_2 \frac{1}{r_{12}} \delta(\vec{r}_2 - \vec{r}') \, \delta_{s''s'}$$

$$+ \sum_{s} \sum_{s''} \int d^3r_2 \bar{\rho}_{s''}(\vec{r}_2) \int d^3r_1 \frac{1}{r_{12}} \delta(\vec{r}_1 - \vec{r}') \, \delta_{ss'}$$

$$= \sum_{s} \int d^3r_1 \, \bar{\rho}_s(\vec{r}_1)/|\vec{r}_1 - \vec{r}'| + \sum_{s''} \int d^3r_2 \, \bar{\rho}_{s''}(\vec{r}_2)/|\vec{r}' - \vec{r}_2|$$

$$= \sum_{s} \int d^3r_1 \, 2\bar{\rho}_s(\vec{r}_1)/|\vec{r}_1 - \vec{r}'|$$

$$= \int d^3r_1 \, 2 \, \bar{\rho}(\vec{r}_1)/|\vec{r}_1 - \vec{r}'| = V_c(\bar{\rho}, \vec{r}') \tag{A.9}$$

Finally, let us consider the exchange-correlation energy term $\bar{U}_{ex}$. From equation (A.1), we have:

$$\frac{\delta \bar{U}_{ex}}{\delta \bar{\rho}_{s'}(\vec{r}')} = \frac{\delta}{\delta \bar{\rho}_{s'}(\vec{r}')} C_\alpha \int \{ \sum_{s} \bar{\rho}_s(\vec{r}_1)^{4/3} \} \, d^3r_1$$

$$= C_\alpha \sum_{s} \int (4/3) \, \bar{\rho}_s(\vec{r}_1)^{1/3} \, \delta(\vec{r}_1 - \vec{r}') \, \delta_{ss'} \, d^3r_1$$

$$= (4/3) \, C_\alpha \, \bar{\rho}_{s'}(\vec{r}')^{1/3} \tag{A.10}$$

Combining equations (A.8), (A.9), (A.10) and substituting into equation (A.6):

$$\delta \bar{U}_T = \sum_{s'} \int d^3r \, \tilde{u}_i(\vec{r}) \int d^3r' \, \{ V_{ne}(\vec{r}') + V_c(\bar{\rho}, \vec{r}') + \frac{4}{3} C_\alpha \bar{\rho}_{s'}(\vec{r}')^{1/3} \}$$

$$\times \ \frac{\delta \bar{\rho}_{s'}(\vec{r}\,')}{\delta \hat{u}_i^*(\vec{r})} \ + \ (c.c.) \tag{A.11}$$

Since we have two different forms for $\delta \bar{\rho}_{s'}(\vec{r}\,')/\delta \hat{u}_i^*(\vec{r})$ depending on the location of $\vec{r}\,'$, as expressed in in equation (A.7), we separate the integral over $\vec{r}\,'$ into two parts, one over the atomic regions ($\beta = 0, 1, \ldots N$) and the other over the intersphere region II:

$$\delta \bar{U}_T = \sum_{s'} \int d^3 r \ \delta \hat{u}_i^*(\vec{r}) \{ \sum_{\beta=0}^{N} \int_\beta d^3 r' \ \frac{\delta \bar{\rho}_{s'}(\vec{r}_\beta')}{\delta \hat{u}_i^*(\vec{r})} \ \{ \bar{V}_{ne}(r_\beta') + V_c(\bar{\rho}, r_\beta')$$

$$+ \frac{4}{3} C_\alpha \ \bar{\rho}_{s'}(\vec{r}_\beta')^{1/3} \} \ + \ \int_{II} d^3 r' \ \frac{\delta \bar{\rho}_{s'}(\vec{r}\,')}{\delta \hat{u}_i^*(\vec{r})} \ \{ \ \bar{V}_{ne,II}$$

$$+ V_c(\bar{\rho}, \vec{r}\,') + \frac{4}{3} C_\alpha \ \bar{\rho}_{II,s'} \} \} \ + \ (c.c.)$$

By equation (A.7), we have:

$$\delta \bar{U}_T = \sum_{s'} \int d^3 r \ \hat{u}_i^*(\vec{r}) \{ \sum_{\beta=0}^{N} \int_\beta d^3 r' \ \{ 1/(4\pi) \ n_i \delta_{s_i s'}$$

$$\times \ \delta(\vec{r} - \vec{r}_\beta') \hat{u}_i(\vec{r}_\beta') d\Omega_\beta' \} \ \{ \bar{V}_{ne}(\vec{r}_\beta') + V_c(\bar{\rho}, \vec{r}_\beta') + (4/3) C_\alpha \bar{\rho}_{s'}(\vec{r}_\beta')^{1/3} \}$$

$$+ \ \int_{II} d^3 r' \{ \frac{1}{V_{II}} \ n_i \ \delta_{s_i s'} \int_{II} \delta(\vec{r} - \vec{r}\,'') \hat{u}_i(\vec{r}\,'') d^3 r'' \} \{ \bar{V}_{ne,II}$$

$$+ V_c(\bar{\rho}, \vec{r}\,') + (4/3) C_\alpha \bar{\rho}_{II,s'}^{1/3} \} \} \ + \ (c.c.)$$

Integrating over $\vec{r}$, we have:

$$\delta \bar{U}_T = \sum_{\beta=0}^{N} \int_{\beta} d^3 r'_\beta \ (1/4\pi) \ n_i \ \{ \int \delta \tilde{u}_i^*(\vec{r}')\tilde{u}_i(\vec{r}')d\Omega'_\beta \}$$

$$\times \ \{\bar{V}_{ne}(r'_\beta)+V_c(\bar{\rho},\vec{r}'_\beta)+(4/3)C_\alpha \bar{\rho}_{s_i}(r'_\beta)^{1/3}\}$$

$$+ \int_{II} d^3 r' \ \frac{1}{V_{II}} \ n_i \ \int_{II} \delta \tilde{u}_i^*(\vec{r}'')\tilde{u}_i(\vec{r}')d^3 r''$$

$$\times \ \{\bar{V}_{ne,II}+V_c(\bar{\rho},\vec{r}')+(4/3)C_\alpha \bar{\rho}_{II,s_i}^{1/3}\}+ \ (c.c.)$$

$$= \sum_{\beta=0}^{N} \int_{\beta} r_\beta'^2 dr'_\beta d\Omega'_\beta \ n_i/(4\pi)\{ \ \bar{V}_{ne}(r'_\beta)+V_c(\bar{\rho},\vec{r}'_\beta)+ \frac{4}{3}C_\alpha \bar{\rho}_{s_i}(r'_\beta)^{1/3}\}$$

$$\times \{ \ \int d\Omega'_\beta \ \delta \tilde{u}_i^*(\vec{r}'_\beta)\tilde{u}_i(\vec{r}'_\beta)\} + \int_{II} d^3 r'' \ \delta \tilde{u}_i^*(\vec{r}'')\tilde{u}_i(\vec{r}'')\frac{1}{V_{II}} \ n_i$$

$$\times \ \int_{II} d^3 r'\{ \ \bar{V}_{ne,II}+V_c(\bar{\rho},\vec{r}')+ \frac{4}{3}C_\alpha \bar{\rho}_{II,s_i}^{1/3}\} \ + \ (c.c.)$$

$$= \sum_{\beta=0}^{N} \ n_i/(4\pi) \int_{\beta} r_\beta'^2 dr'_\beta \ \{ \ \int d\Omega'_\beta \ \bar{V}_{ne}(r'_\beta)+V_c(\bar{\rho},\vec{r}'_\beta)$$

$$+ \ (4/3)C \ \bar{\rho}_{s_i}(r'_\beta)^{1/3} \ \}\times \{ \ \int d\Omega'_\beta \delta \tilde{u}_i(\vec{r}'_\beta)\tilde{u}_i(\vec{r}'_\beta)\}$$

$$+ \ \int_{II} d^3 r'' \ \delta \tilde{u}_i^*(\vec{r}'')\tilde{u}_i(\vec{r}'') \ \frac{1}{V_{II}} \ n_i \int_{II}\{\bar{V}_{ne,II}+V_c(\bar{\rho},\vec{r}')$$

$$+ \ (4/3)C_\alpha \bar{\rho}_{II,s_i}^{1/3}\} \qquad + \ (c.c.) \qquad\qquad (A.12)$$

Since the muffin-tin average of a function f is defined as:

$$\bar{f}(\vec{r}) = \begin{cases} 1/(4\pi)\int d\Omega \ f(\vec{r}) & \text{if } \vec{r} \text{ in the atomic regions} \\ 1/V_{II}\int_{II} d^3 r \ f(\vec{r}) & \text{if } \vec{r} \text{ in the intersphere region} \end{cases}$$

So, equation (A.12) is reduced to:

$$\delta \overline{U}_T = \sum_{\beta=0}^{N} n_i/(4\pi) \int_{\beta} r_{\beta}' dr_{\beta}' \ \{4\pi \overline{V}_{ne}(r_{\beta}') + 4\pi \overline{V}_c(\overline{\rho}, r_{\beta}')$$

$$+ 4\pi(4/3)C_\alpha \overline{\rho}_{s_i}(r_{\beta}')\}\{ \int d\Omega_{\beta}' \ \tilde{u}_i(\vec{r}_{\beta}') \ \tilde{u}_i^*(\vec{r}_{\beta}')\}$$

$$+ n_i/V_{II} \int_{II} d^3 r'' \ \delta \tilde{u}_i^*(\vec{r}'') \tilde{u}_i(\vec{r}'') \ \{V_{II}\overline{V}_{ne,II} + V_{II}\overline{V}_{c,II}(\overline{\rho})$$

$$+ 4\pi(4/3)C_\alpha \overline{\rho}_{II,s_i}\} \quad + \quad (c.c.)$$

$$= \sum_{\beta=0}^{N} n_i \int_{\beta} d^3 r_{\beta}' \ \delta \tilde{u}_i^*(\vec{r}_{\beta}')\{ \ \overline{V}_{ne}(r_{\beta}') + \overline{V}_c(\overline{\rho}, r_{\beta}')$$

$$+ (4/3)C_\alpha \overline{\rho}_{s_i}(r_{\beta}')^{1/3}\} \ \tilde{u}_i(\vec{r}_{\beta}') + n_i \int_{II} d^3 r'' \delta \tilde{u}_i^*(\vec{r}'')\{ \ \overline{V}_{ne,II}$$

$$+ \overline{V}_{c,II} + (4/3)C_\alpha \overline{\rho}_{II,s_i}^{1/3}\} \ \tilde{u}_i(\vec{r}'') + (c.c.)$$

Therefore, $$\delta \overline{U}_T = \int d^3 r \ n_i \ \delta u_i^*(\vec{r})\{ \ \overline{V}_{ne}(\vec{r}) + \overline{V}_c(\overline{\rho}, \vec{r})$$

$$+ (4/3)C_\alpha \overline{\rho}_{s_i}(\vec{r})^{1/3}\} \ \tilde{u}_i(\vec{r}) + (c.c.) \quad (A.13)$$

Thus, combining with the kinetic energy part in equation (A.5), we have:

$$\delta \overline{\langle E_{x_\alpha}(\overline{\rho}) \rangle} = \int d^3 r \ n_i \ \tilde{u}_i^*(\vec{r}) \ \{-\nabla^2 + \overline{V}_{ne}(\vec{r}) + \overline{V}_c(\overline{\rho}, \vec{r})$$

$$+ \frac{4}{3}C_\alpha \overline{\rho}_{s_i}(\vec{r})^{1/3}\} \ \tilde{u}_i(\vec{r}) + (c.c.) \quad (A.14)$$

Since we have the restraints on $\tilde{u}_i$ imposed by the orthonormality conditions, we have to introduce the Lagrange multipliers λ_{ij} and demand that

$$\delta \{\overline{<E_{x\alpha}(\overline{\rho})>} + \sum_i \sum_j n_i^{\frac{1}{2}} n_j^{\frac{1}{2}} \lambda_{ij} \int \tilde{u}_i^*(\vec{r}) \tilde{u}_j(\vec{r}) \, d^3r\} = 0$$

where we introduce a factor $n_i^{\frac{1}{2}} n_j^{\frac{1}{2}}$ with each λ_{ij} for the convenience of the derivation.

Since $\delta \{ \sum_i \sum_j n_i^{\frac{1}{2}} n_j^{\frac{1}{2}} \lambda_{ij} \int \tilde{u}_i^*(\vec{r}) \tilde{u}_j(\vec{r}) \, d^3r\}$

$$= \sum_j n_i^{\frac{1}{2}} n_j^{\frac{1}{2}} \lambda_{ij} \int \delta\tilde{u}_i^*(\vec{r}) \tilde{u}_j(\vec{r}) d^3r \quad + \quad (c.c.)$$

therefor, together with equation (A.14), we have:

$$\int d^3r \, \delta\tilde{u}_i^*(\vec{r}) \, \{n_i\{ -\nabla^2 + \overline{V}_{ne}(\vec{r}) + \overline{V}_c(\overline{\rho},\vec{r}) + \frac{4}{3} C_\alpha \overline{\rho}_{s_i}(\vec{r})^{1/3}\}$$

$$\times \tilde{u}_i(\vec{r}) + n_i^{\frac{1}{2}} \sum_j n_j^{\frac{1}{2}} \lambda_{ij} \tilde{u}_j(\vec{r})\} \quad + \quad (c.c.) \quad = \quad 0 \qquad (A.15)$$

If the first part of equation (A.15) is equal to zero, so will be its complex conjugate. Thus we can drop the complex conjugate term. Also, since $\delta\tilde{u}_i^*(\vec{r})$ is arbitrary, therefore, the necessary and sufficient condition for $\overline{<E_{x\alpha}(\overline{\rho})>}$ to be stable is that $\tilde{u}_i$ satisfy:

$$\{-\nabla^2 + \overline{V}_{ne}(\vec{r}) + \overline{V}_c(\overline{\rho},\vec{r}) + \frac{4}{3} C_\alpha \overline{\rho}_{s_i}(\vec{r})^{1/3}\} n_i^{\frac{1}{2}} \tilde{u}_i(\vec{r}) = -\sum_j \lambda_{ij} n_j^{\frac{1}{2}} \tilde{u}_j(\vec{r})$$

$$(A.16)$$

Since the λ_{ij} matrix is hermitian, it may be diago-
nalized by some unitary transformation C:

$$n_i^{\frac{1}{2}} \tilde{u}_i' = \sum_j C_{ij}\, n_j^{\frac{1}{2}}\, \tilde{u}_j$$

or, in matrix form: $\mathbf{n}^{\frac{1}{2}}\, \tilde{\mathbf{u}}' = \mathbb{C}\, \mathbf{n}^{\frac{1}{2}}\, \tilde{\mathbf{u}}$

It can be easily shown that the density formed from
$\tilde{u}_i'$ is invariant for such unitary transformation. Hence, the
operator H(ρ) on the LHS of equation (A.16) remains as
the same form after the transformation, i.e., $\mathbb{C}\mathbb{H}(\rho)\mathbb{C}^{\dagger}=\mathbb{H}(\rho')$.

Writing equation (A.16) in matrix form:

$$\mathbb{H}(\rho)\, \mathbf{n}^{\frac{1}{2}}\, \tilde{\mathbf{u}} = -\,\lambda\, \mathbf{n}^{\frac{1}{2}}\, \tilde{\mathbf{u}}$$

Multiplying both sides by $\mathbb{C}$ and inserting $\mathbb{C}^{\dagger}\mathbb{C}$(which is equal
to identity because $\mathbb{C}$ is unitary) in between $\mathbb{H}$ and $\mathbf{n}^{\frac{1}{2}}$ on the
LHS and in between λ and $\mathbf{n}^{\frac{1}{2}}$ on the RHS, we have:

$$\mathbb{C}\, \mathbb{H}(\rho)\, \mathbb{C}^{\dagger}\, \mathbb{C}\, \mathbf{n}^{\frac{1}{2}}\, \tilde{\mathbf{u}} = -\,\mathbb{C}\, \lambda\, \mathbb{C}^{\dagger}\, \mathbb{C}\, \mathbf{n}^{\frac{1}{2}}\, \tilde{\mathbf{u}}$$

which implies $\quad \mathbb{H}(\rho')\, \mathbf{n}^{\frac{1}{2}}\, \tilde{\mathbf{u}}' = -\,\lambda'\, \mathbf{n}^{\frac{1}{2}}\, \tilde{\mathbf{u}}'$

Now, since λ' is diagonal, therefore $\lambda_{ij}' = \delta_{ij}\, \tilde{\varepsilon}_i'$. Thus,

$$\{-\nabla^2 + \overline{V}_{ne}(\vec{r}) + \overline{V}_c(\overline{\rho}',\vec{r}) + \tfrac{4}{3}C_\alpha \overline{\rho}_{s_i}'(\vec{r})^{1/3}\}\, \tilde{u}_i'(\vec{r}) = \tilde{\varepsilon}_i'\, \tilde{u}_i'(\vec{r})$$

which is the muffin-tin Xα one-electron equations.

APPENDIX B

THE MULTIPLE SCATTERING METHOD

To solve the muffin-tin approximate Xα one-electron equations, we can employ the multiple scattering method which is commonly used in scattering problems. Starting with the equation:

$$\{-\nabla^2 + \overline{V}_{x\alpha}(\overline{\rho}, \vec{r})\} \; \tilde{u}_i(\vec{r}) = \tilde{\epsilon}_i \tilde{u}_i(\vec{r}) \qquad (B.1)$$

we have, in the atomic regions:

$$\{-\nabla^2 + \overline{V}_{x\alpha}(\overline{\rho}, r_\beta)\} \; \tilde{u}_i(\vec{r}_\beta) = \tilde{\epsilon}_i \; \tilde{u}_i(\vec{r}_\beta)$$

The solutions inside the sphere β can be expanded in a partial wave expansion:

$$\tilde{u}_i(\vec{r}_\beta) = \sum_{\ell, m} C_{\ell m}^{i\beta} \, R_\ell(r_\beta, \tilde{\epsilon}_i) \, Y_\ell^m(\vec{r}_\beta) \qquad (B.2)$$

where we have used the real spherical harmonics and the radial functions R_ℓ have to satisfy the following differential equations:

130

$$\{-\frac{1}{r_\beta{}^2}\frac{d}{dr_\beta}(r_\beta{}^2\frac{d}{dr_\beta}) + \ell(\ell+1)/r_\beta{}^2 + \overline{V}_{x\alpha}(\overline{\rho},r_\beta)\} R_\ell(r_\beta,\overset{\sim}{\varepsilon})$$

$$= \overset{\sim}{\varepsilon}_i R_\ell(r_\beta,\overset{\sim}{\varepsilon}_i)$$

In the intersphere region II, the potential is a constant $\overline{V}_{II}$. Thus equation (B.1) is reduced to:

$$\{ - \nabla^2 + (\overline{V}_{II} - \overset{\sim}{\varepsilon}_i)\} \tilde{u}_i(\vec{r}) = 0$$

which is just the equation for a free electron. Hence we may express $\tilde{u}_i$ in this region as a multicenter partial wave expansion:

$$\tilde{u}_i(\vec{r}) = \left[\begin{array}{l} \displaystyle\sum_{\beta=1}^{N} \sum_{\ell,m} A_{\ell m}^{i\beta} \eta_\ell(\kappa r_\beta) Y_\ell^m(\vec{r}_\beta) + \sum_{\ell,m} A_{\ell m}^{i0} j_\ell(\kappa r_0) Y_\ell^m(\vec{r}_0) \\ \qquad\qquad\qquad\qquad\qquad\qquad \text{if } \overset{\sim}{\varepsilon} > V_{II} \\[2em] \displaystyle\sum_{\rho=1}^{N} \sum_{\ell,m} A_{\ell m}^{i\beta} k_\ell(\kappa r_\beta) Y_\ell^m(\vec{r}_\beta) + \sum_{\ell,m} A_{\ell m}^{i0} i_\ell(\kappa r_0) Y_\ell^m(\vec{r}_0) \\ \qquad\qquad\qquad\qquad\qquad\qquad \text{if } \overset{\sim}{\varepsilon} < V_{II} \end{array} \right. \tag{B.3}$$

where $\kappa = (| V_{II} - \varepsilon_i |)^{\frac{1}{2}}$

η_ℓ, j_ℓ are respectively the ordinary spherical Neumann and Bessel functions: k_ℓ and i_ℓ are respectively the modified spherical Hankel functions and Bessel functions.

With the requirements that the spin-orbitals $\tilde{u}_i$ and their first derivatives have to be continuous on the surfaces of the different spheres, the C-coefficients and A-coefficents

can be determined. The method is to express each of the partial waves, $\eta_\ell(\kappa r_\beta)Y_\ell^m(\vec{r}_\beta)$, $j_\ell(\kappa r_0)Y_\ell^m(\vec{r}_0)$ etc. of different centers, in terms of partial waves all centered at one sphere α, and then join smoothly with the $\tilde{u}_i$ as expressed in equation (B.2) inside the sphere α, and similarly, for the derivatives. The result is that the C and A-coefficients are related by the following equations:

$$
A_{\ell m}^{i\alpha} = \begin{cases} \kappa b_\alpha^2 \left[\, j_\ell(\kappa b_\alpha), R_\ell(b_\alpha, \tilde{\varepsilon}_i)\right] C_{\ell m}^{i\alpha} \, , & \tilde{\varepsilon}_i > \overline{V}_{II} \\[2ex] (-1)^{\ell+1} \kappa b_\alpha^2 \left[\, i_\ell(\kappa b_\alpha), R_\ell(b_\alpha, \tilde{\varepsilon}_i)\right] C_{\ell m}^{i\alpha}, & \tilde{\varepsilon}_i < \overline{V}_{II} \end{cases}
$$

$$\text{(B.4)}$$

$$
A_{\ell m}^{i0} = \begin{cases} \kappa b_0^2 \left[R_\ell(b_0, \tilde{\varepsilon}_i), \eta_\ell(\kappa b_0)\right] C_{\ell m}^{i0} & \tilde{\varepsilon}_i > \overline{V}_{II} \\[2ex] (-1)^{\ell+1} \kappa b_0^2 \left[R_\ell(b_0, \tilde{\varepsilon}_i), k_\ell(\kappa b_0)\right] C_{\ell m}^{i0} & \varepsilon_i < \overline{V}_{II} \end{cases}
$$

where b_α are the radius of sphere α,

$[u,v]$ are the Wronskian defined as $u\dfrac{dv}{dx} - v\dfrac{du}{dx}$.

Also, we obtain a set of equations for the A-coefficients:

$$
(t_\ell(\tilde{\varepsilon}_i))^{-1} A_{\ell m}^i = \sum_{\substack{\beta=0 \\ \beta \neq \alpha}}^{N} \sum_{\ell'm'} G_{\ell m, \ell'm'}(R_{\alpha\beta}, \tilde{\varepsilon}_i) A_{\ell'm'}^i \tag{B.5}
$$

where $R_{\alpha\beta}$ are the distance between the centers of sphere α and sphere β; and the t and G-coefficeints are defined as below:

$$
t_\ell^\alpha(\varepsilon) = \begin{cases}
- [j_\ell(\kappa b_\alpha), R_\ell(b_\alpha,\varepsilon)] / [\eta_\ell(\kappa b_\alpha), R_\ell(b_\alpha,\varepsilon)] & \varepsilon > \overline{V}_{II} \\[2em]
- [i_\ell(\kappa b_\alpha), R_\ell(b_\alpha,\varepsilon)] / \{k_\ell(\kappa b_\alpha), R_\ell(b_\alpha,\varepsilon)\} & \varepsilon < \overline{V}_{II}
\end{cases}
$$

$$
t_\ell(\varepsilon) = \begin{cases}
- [\eta_\ell(\kappa b_0), R_\ell(b_0,\varepsilon)] / [j_\ell(\kappa b_0), R_\ell(b_0,\varepsilon)] & \varepsilon > \overline{V}_{II} \\[2em]
- [k_\ell(\kappa b_0), R_\ell(b_0,\varepsilon)] / [i_\ell(\kappa b_0), R_\ell(b_0,\varepsilon)] & \varepsilon < \overline{V}_{II}
\end{cases}
$$

(B.6)

$$
G_{\ell m, \ell'm'}^{\alpha\beta}(R_{\alpha\beta},\varepsilon) = \begin{cases}
(1-\delta_{\alpha\beta})4\pi i^{\ell-\ell'} \sum_{\ell''m''} i^{-\ell''} I(\ell''m'';\ell m;\ell'm') \\[1em]
\times\, \eta_{\ell''}(\kappa R_{\alpha\beta})Y_{\ell''}^{m''}(\vec{R}_{\alpha\beta}) & \varepsilon > \overline{V}_{II} \\[1.5em]
(1-\delta_{\alpha\beta})4\pi(-1)^{\ell+\ell'} \sum_{\ell''m''} I(\ell'm';\ell m;\ell'm') \\[1em]
\times\, k_{\ell''}(\kappa R_{\alpha\beta})Y_{\ell''}^{m''}(\vec{R}_{\alpha\beta}) & \varepsilon < \overline{V}_{II}
\end{cases}
$$

$$
G_{\ell m, \ell'm'}^{\alpha 0}(R_{\alpha 0},\varepsilon) = \begin{cases}
4\pi i^{\ell-\ell'} \sum_{\ell''m''} i^{-\ell''} I(\ell''m'';\ell m;\ell'm') \\[1em]
\times\, j_{\ell''}(\kappa R_{\alpha 0})Y_{\ell''}^{m''}(\vec{R}_{\alpha 0}) & \varepsilon > \overline{V}_{II} \\[1.5em]
4\pi(-1)^{\ell+\ell'} \sum_{\ell''m''} I(\ell''m'';\ell m;\ell'm') \\[1em]
\times\, i_{\ell''}(\kappa R_{\alpha 0})Y_{\ell''}^{m''}(\vec{R}_{\alpha 0}) & \varepsilon < \overline{V}_{II}
\end{cases}
$$

(B.7)

where $I(\ell''m'';\ell m;\ell'm')$ are the Gaunt coefficients defined for the real spherical harmonics as:

$$I(\ell''m'; \ell m; \ell'm') = \int Y_{\ell''}^{m''}(\vec{r}) Y_{\ell}^{m}(\vec{r}) Y_{\ell'}^{m'}(\vec{r}) \, d\Omega$$

From equation (B.5), we see that we have nontrivial solutions for the A-coefficients and hence for the C-coefficients only when

$$\det \left| t_{\ell}^{\alpha}(\tilde{\epsilon}_i)^{-1} \delta_{\alpha\beta} \delta_{\ell\ell'} \delta_{mm'} - G_{\ell m, \ell'm'}^{\alpha\beta}(R_{\alpha\beta}, \tilde{\epsilon}_i) \right| = 0 \qquad (B.8)$$

Thus we can find the eigenvalues $\tilde{\epsilon}_i$ by finding the zeroes of the determinant (B.8), and from this we can find the C and A-coefficients, and hence the wavefunction $\tilde{u}_i$, by equations (B.5) and (B.4). Here we notice that the functions $t_{\ell}^{\alpha}(\epsilon)$ depend on the value of $\kappa = |\tilde{\epsilon} - \bar{V}_{II}|^{\frac{1}{2}}$ and the value of the radial function R_{ℓ} and its derivative on the boundary of the sphere, and therefore implicitly on the potential. The G-coefficients also depend on $\tilde{\epsilon}$ and the potential through the quantity κ. Hence the determinant in equation (B.8) is nonlinear in $\tilde{\epsilon}$. The way we determine the eigenvalues $\tilde{\epsilon}_i$ is to compute the determinant over a range of $\tilde{\epsilon}$ that bracketed the guessed eigenvalues $\tilde{\epsilon}_i$. The value of the determinant changes sign on the two sides of the guessed $\tilde{\epsilon}_i$. Then we inversely interpolate the values to find the zero, and hence the eigenvalue $\tilde{\epsilon}_i$, of the determinant.

HELLMANN-FEYNMAN THEOREM AND THE Xα WAVEFUNCTIONS[*]

In Chapter II and Chapter III, we mentioned that the exact Xα wavefunctions, for the case where α is constant everywhere, rigorously obey the Hellmann-Feynman theorem. We present a proof in this appendix.

Starting with the expression for the exact Xα total energy in equation (2.1):

$$\langle E_{x\alpha} \rangle = \sum_i n_i \int u_i^*(\vec{r}_1)(-\nabla_1)u_i(\vec{r}_1)d^3r_1$$

$$+ \int \sum_{p=1}^{N} \frac{-2Z_p}{|\vec{r}_1 - \vec{R}_p|} \rho(\vec{r}_1)d^3r_1 + \frac{1}{2} \int\int \frac{2\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d^3r_1 d^3r_2$$

$$+ \frac{1}{2} \int \rho_\uparrow(\vec{r}_1)U_{x\alpha\uparrow}(\vec{r}_1)d^3r_1 + \frac{1}{2} \int \rho_\downarrow(\vec{r}_1)U_{x\alpha\downarrow}(\vec{r}_1)d^3r_1$$

$$+ \frac{1}{2} \sum_{\substack{p,q \\ p \neq q}} 2Z_p Z_q / R_{pq} \tag{C.1}$$

where the energy is in Rydbergs and the distances are in atomic units. Also,

$$U_{x\alpha,s}(\vec{r}) = -9\alpha \left\{ 3/(4\pi) \rho_s(\vec{r})^{1/3} \right\} \qquad s = \uparrow \text{ and } \downarrow$$

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[*] The main reference for this appendix is J.C. Slater (1972b).

$$\rho(\vec{r}) = \rho_\uparrow(\vec{r}) + \rho_\downarrow(\vec{r}) = \sum_i n_i u_i^*(\vec{r}) u_i(\vec{r}) \qquad (C.2)$$

Now we differentiate both sides of equation (C.1) with respect to X_p, the X coordinate of the pth nucleus. Then if we forget that the spin-orbitals u_i, and hence the charge density ρ, depend on the nuclear positions implicitly, we will get:

$$- \frac{\partial \langle E_{x\alpha} \rangle}{\partial X_p} = \int \rho(\vec{r}_1) \frac{\partial}{\partial X_p} \left(\frac{2Z_p}{|\vec{r}_1 - \vec{R}_p|} \right) d^3 r_1 - \sum_{q \neq p} \frac{\partial}{\partial X_p} \left(\frac{2Z_p}{|\vec{R}_p - \vec{R}_q|} \right)$$

$$(C.3)$$

which is what the Hellmann-Feynman Theorem contains if u_i and $\langle E \rangle$ are derived from the exact hamiltonian instead of the Xα hamiltonian (C.1). We may wonder that the fact that we forgot the dependence of u_i on X_p would cause some errors. However, we show in the following that, in the case that α is constant everywhere, the terms arising from this omission just cancel each other, and thus equation (C.3) exactly holds. To show this, we consider the omitted terms F_{omit}:

$$F_{omit} = \sum_i n_i \int \left\{ \frac{\partial u_i^*(\vec{r}_1)}{\partial X_p} (-\nabla_1^2) u_i(\vec{r}_1) + u_i^*(\vec{r}_1)(-\nabla_1^2) \frac{\partial u_i}{\partial X_p} \right\} d^3 r_1$$

$$+ \int \sum_{p=1}^{N} \frac{-2Z_p}{|\vec{r}_1 - \vec{R}_p|} \frac{\partial \rho(\vec{r}_1)}{\partial X_p} d^3 r_1 + \frac{1}{2} \int d^3 r_1 \rho(\vec{r}_1) \int d^3 r_2 \frac{2}{r_{12}} \frac{\partial \rho(\vec{r}_2)}{\partial X_p}$$

$$+ \frac{1}{2} \int d^3 r_2 \rho(\vec{r}_2) \int d^3 r_1 \frac{2}{r_{12}} \frac{\partial \rho(\vec{r}_1)}{\partial X_p}$$

$$- \frac{9}{2} \alpha (3/4\pi)^{1/3} \sum_{s} \int \frac{\partial}{\partial X_p} (\rho \ (\vec{r} \ )^{4/3}) \ d^3 r_1$$

Since $\qquad \rho(\vec{r}) = \sum_j n_j u_j^*(\vec{r}) u_j(\vec{r})$

therefore $\qquad \frac{\partial \rho(\vec{r})}{\partial X_p} = \sum_i \ (\ \frac{\partial \rho}{\partial u_i} \frac{\partial u_i}{\partial X_p} \quad \frac{\partial \rho}{\partial u_i^*} \frac{\partial u_i^*}{\partial X_p} \ )$

$$= \sum_i \{ \ n_i u_i^*(\vec{r}) \frac{\partial u_i}{\partial X_p} + n_i u_i(\vec{r}) \frac{\partial u_i^*}{\partial X_p} \ \} \qquad (C.4)$$

Hence $\qquad F_{omit} = \sum_i n_i \int \frac{\partial u_i^*(\vec{r}_1)}{\partial X_p} \{ - \nabla_1^2 + \sum_{p=1}^{N} \frac{-2 Z_p}{|\vec{r}_1 - \vec{R}_p|}$

$$+ \frac{1}{2} \int d^3 r_3 \rho(\vec{r}_3) \frac{2}{r_{13}} + \frac{1}{2} \int d^3 r_2 \rho(\vec{r}_2) \frac{2}{r_{12}}$$

$$- \frac{9}{2} \alpha (3/4\pi)^{1/3} (4/3) \rho_{s_i}(\vec{r}_1)^{1/3} \} \ u_i(\vec{r}_1) \ d^3 r_1$$

$$+ \quad \text{(complex conjugate)}$$

We note that the term inside the bracket together with $u_i(\vec{r}_1)$ in the above equation is just as the following:

$$\{ - \nabla_1^2 + \sum_{p=1}^{N} \frac{-2 Z_p}{|\vec{r}_1 - \vec{R}_p|} + \int \frac{2 \rho(\vec{r}_2)}{r_{12}} d^3 r_2 - 6 \alpha (3/4\pi)^{\frac{1}{3}} \rho_{s_i}(\vec{r}_1)^{\frac{1}{3}} \}$$

$$\times \ u_i(\vec{r}_1)$$

From equation (2.4), we see that it is just equal to $\varepsilon_i u_i(\vec{r}_1)$. Hence, we have:

$$F_{omit} = \sum_i n_i \int \frac{\partial u_i^*(\vec{r}_1)}{\partial X_p} \epsilon_i u_i(\vec{r}_i) d^3r_1 + (\text{complex conjugate})$$

$$= \sum_i n_i \epsilon_i \frac{\partial}{\partial X_p} \int u_i^*(\vec{r}_1) u_i(\vec{r}_1) d^3r_1$$

On account of the normalization of u_i, we have:

$$\frac{\partial}{\partial X_p} \left\{ \int u_i^*(\vec{r}_1) u_i(\vec{r}_1) d^3r_1 \right\} = 0$$

Hence, $\quad F_{omit} = 0$

One small point about this derivation is that in equation (C.4), we had implicitly assumed the value α is constant everywhere so that $\frac{\partial \alpha}{\partial X_p} = 0$ and so $\frac{\partial \rho}{\partial X_p}$ does not involve the term $\frac{\partial \rho}{\partial \alpha}$. This assumption of constant α does not cause any trouble if we are considering a molecule formed from a single type of atoms, such as a homonuclear diatomic molecule. However, some corrections have to be made in the treatment of a molecule formed from different types of atoms.

PROOF OF THE INDEPENDENCE OF DIPOLE MOMENT
ON THE CHOICE OF THE ORIGIN FOR A NEUTRAL MOLECULE

In Chapter III and Chapter V, we claim that for a neutral molecular system the value of the dipole moment is independent of the choice of the origin of the coordinates, so that we can locate the origin at the center of the outer sphere. We shall prove it in the following:

The dipole moment $\vec{\mu}$ computed with reference to an origin 0 is defined as:

$$\vec{\mu} = \sum_i Z_i \vec{R}_i - \int \rho(\vec{r})\vec{r} \; d^3r \qquad (D.1)$$

where $\rho(\vec{r})$ is the electronic density distribution,

Z_i are the atomic numbers of the nuclei,

$\vec{R}_i$ are the position vectors of the nuclei with the origin at 0, similarly for the electronic coordinate $\vec{r}$.

Now, suppose the origin of the coordinate system is removed to 0' by the transformation $\vec{T}$ (figure D.1). Then the dipole moment $\vec{\mu}'$ computed with reference to 0' is:

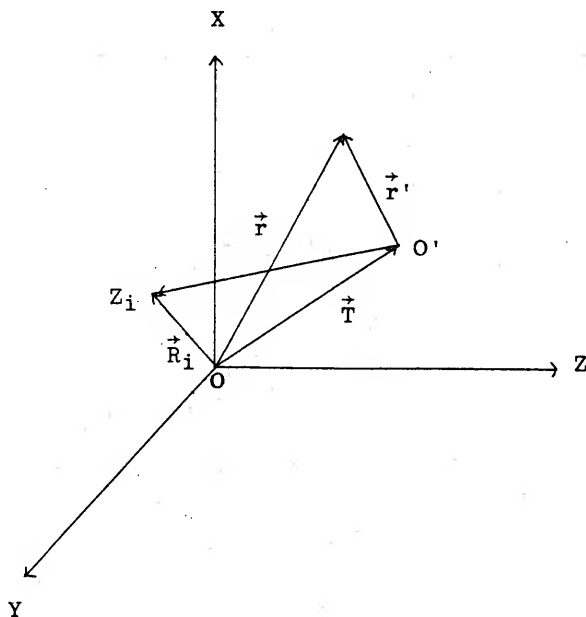$$\vec{\mu}' = \sum_i Z_i \vec{R}_i' - \int \rho(\vec{r}')\vec{r}' \; d^3r' \qquad (D.2)$$

139

Fig. D.1   Transformation of Coordinates

where $\vec{R}'_i$ and $\vec{r}'$ are measured with respect to the origin O'.

From figure (D.1) we see:

$$\vec{R}'_i = \vec{R}_i - \vec{T} \qquad \text{and} \qquad \vec{r}' = \vec{r} - \vec{T}$$

Substituting in equation (D.2), we have:

$$\vec{\mu}' = \sum_i Z_i(\vec{R}_i - \vec{T}) - \int \rho(\vec{r}')(\vec{r} - \vec{T})d^3r'$$

$$= \{ Z_i \vec{R}_i - \int \rho(\vec{r}')\vec{r} \, d^3r' \} - \{ \sum_i Z_i - \int \rho(\vec{r}')d^3r' \} \, \vec{T}$$

Since $\vec{r}'$ and $\vec{r}$ are referring to the same point, we have $\rho(\vec{r}') = \rho(\vec{r})$. Hence the term inside the first bracket is equal to $\vec{\mu}$, the dipole moment value computed with respect to O. Also, the term inside the second bracket is equal to the net charge of the system. Since we have a neutral system, the net charge is equal to zero. Thus, we have:

$$\mu' = \mu$$

Since $\vec{T}$ is arbitrary, we have proved that the dipole moment is independent of the choice of the origin for a neutral system.

APPENDIX E

EXPANSION THEOREMS FOR THE BESSEL FUNCTIONS
AND THE NEUMANN FUNCTIONS

Starting from the well known plane-wave expansion:

$$e^{i\vec{k}\cdot\vec{r}} = 4\pi \sum_{\ell,m} i^\ell j_\ell(kr) Y_\ell^m(\vec{r}) Y_\ell^m(\vec{k})$$

where we use real spherical harmonics. Then we express the following plane wave in the two equivalent expansions:

$$e^{i\vec{k}\cdot(\vec{r}_2-\vec{r}_1)} = 4\pi \sum_{\ell',m'} i^{\ell'} j_{\ell'}(k|\vec{r}_2-\vec{r}_1|) Y_{\ell'}^{m'}(\vec{r}_2-\vec{r}_1) Y_{\ell'}^{m'}(\vec{k}) \quad (E.1)$$

$$e^{i\vec{k}\cdot(\vec{r}_2-\vec{r}_1)} = e^{i\vec{k}\cdot\vec{r}_2} e^{-i\vec{k}\cdot\vec{r}_1}$$

$$= 4\pi \sum_{\ell',m'} i^{\ell'} j_{\ell'}(kr_2) Y_{\ell'}^{m'}(\vec{r}_2) Y_{\ell'}^{m'}(\vec{k})$$

$$4\pi \sum_{\ell'',m''} i^{-\ell''} j_{\ell''}(kr_1) Y_{\ell''}^{m''}(\vec{r}_1) Y_{\ell''}^{m''}(\vec{k}) \quad (E.2)$$

Multiplying both sides of equation (D.1) by $Y_\ell^m(\vec{k})$ and integrating over the solid angle Ω_k, we have:

$$\int e^{i\vec{k}\cdot(\vec{r}_2-\vec{r}_1)} Y_\ell^m(\vec{k}) d\Omega_k = 4\pi i^\ell j_\ell(k|\vec{r}_2-\vec{r}_1|) Y_\ell^m(\vec{r}_2-\vec{r}_1) \quad (E.3)$$

142

by the orthonormality of the spherical harmonics. Similarly, for (E.2), we have:

$$\int e^{i\vec{k}\cdot(\vec{r}_2-\vec{r}_1)}Y_\ell^m(\hat{k})d\Omega_k$$

$$= (4\pi)^2 \sum_{\ell',m'} \sum_{\ell'',m''} i^{\ell'-\ell''}I(\ell'm';\ell''m'';\ell m)j_{\ell'}(kr_2)Y_{\ell'}^{m'}(\vec{r}_2)$$

$$\times j_{\ell''}(kr_1)Y_{\ell''}^{m''}(\vec{r}_1) \tag{E.4}$$

Comparing (E.3) with (E.4), we find:

$$j_\ell(k|\vec{r}_2-\vec{r}_1|)Y_\ell^m(\vec{r}_2-\vec{r}_1)$$

$$= 4\pi \sum_{\ell',m'} \sum_{\ell'',m''} i^{\ell'-\ell''-\ell} I(\ell'm';\ell''m'';\ell m) j_{\ell'}(kr_2)Y_{\ell'}^{m'}(\vec{r}_2)$$

$$j_{\ell''}(kr_1)Y_{\ell''}^{m''}(\vec{r}_1) \tag{E.5}$$

which is the expansion for $j_\ell(kr)Y_\ell^m(\vec{r})$.

To derive a similar expansion for $n_\ell(kr)Y_\ell^m(\vec{r})$, we use the well known spherical-wave expansion:

$$e^{ik|\vec{r}_2-\vec{r}_1|}/|\vec{r}_2-\vec{r}_1| = 4\pi \, ik \sum_{\ell,m} h_\ell^1(kr_1)j_\ell(kr_2)Y_\ell^m(\vec{r}_1)Y_\ell^m(\vec{r}_2)$$
$$\text{for } r_1 > r_2 \tag{E.6}$$

where $h_\ell^1(x)$ is the spherical Hankel function of the first kind and is related to j_ℓ and n_ℓ by $h_\ell(x)=j_\ell(x)+in_\ell(x)$. Thus, we have:

$$e^{ik|\vec{r}_2-\vec{r}_1-\vec{r}_3|}/|\vec{r}_2-\vec{r}_1-\vec{r}_3|$$

$$= \begin{cases} 4\pi ik \sum_{\ell,m} h_\ell^1(k|\vec{r}_2-\vec{r}_1|)j_\ell(kr_3)Y_\ell^m(\vec{r}_2-\vec{r}_1)Y_\ell^m(\vec{r}_3), \quad |\vec{r}_2-\vec{r}_1|>r_3 \quad (E.7) \\ \\ 4\pi ik \sum_{\ell,m} h_\ell^1(kr_1)j_\ell(k|\vec{r}_2-\vec{r}_3|)Y_\ell^m(\vec{r}_1)Y_\ell^m(\vec{r}_2-\vec{r}_3), \quad r_1>|\vec{r}_2-\vec{r}_3| \quad (E.8) \end{cases}$$

With the expansion for $j_\ell(k|\vec{r}_2-\vec{r}_3|)Y_\ell^m(\vec{r}_2-\vec{r}_3)$ as expressed in (E.5), it follows from (E.8) that

$$e^{ik|\vec{r}_2-\vec{r}_1-\vec{r}_3|}/|\vec{r}_2-\vec{r}_1-\vec{r}_3|$$

$$=4\pi ik \sum_{\ell,m} h_\ell^1(kr_1)Y_\ell^m(\vec{r}_1)4\pi \sum_{\ell',m'}\sum_{\ell'',m''} i^{\ell'-\ell''-\ell} \ I(\ell'm';\ell''m'';\ell m)$$

$$\times \ j_{\ell'}(kr_2)Y_{\ell'}^{m'}(\vec{r}_2)j_{\ell''}(kr_3)Y_{\ell''}^{m''}(\vec{r}_3) \qquad \text{if } r_1>|\vec{r}_2-\vec{r}_3| \qquad (E.9)$$

If $\vec{r}_1$, $\vec{r}_2$, $\vec{r}_3$ satisfy both conditions in (E.7) and (E.9), i.e. $|\vec{r}_2-\vec{r}_1|>r_3$ and $r_1>|\vec{r}_2-\vec{r}_3|$ then we can combine (E.7) and (E.9) together, and after rearranging the dummy summation index in (E.9) and equating the coefficients of $j_\ell(kr_3)Y_\ell^m(\vec{r}_3)$, we have the following identity:

$$h_\ell^1(k|\vec{r}_2-\vec{r}_1|)Y_\ell^m(\vec{r}_2-\vec{r}_1)$$

$$= 4\pi \sum_{\ell'',m''} h_{\ell''}(kr_1)Y_{\ell''}^{m''}(\vec{r}_1) \sum_{\ell',m'}i^{\ell'-\ell-\ell''} \ I(\ell'm';\ell m;\ell''m')$$

$$\times \ j_{\ell'}(kr_2)Y_{\ell'}^{m'}(\vec{r}_2) \qquad \text{if } |\vec{r}_2-\vec{r}_1|>r_3 \text{ and } r_1>|\vec{r}_2-\vec{r}_3| \qquad (E.10)$$

Since $h_\ell^1 = j_\ell + i n_\ell$, and j_ℓ satisfies the same expansion theorem as in (E.10), thus we have the expansion theorem for the Neumann function:

$$n_\ell(k|\vec{r}_2 - \vec{r}_1|) Y_\ell^m(\vec{r}_2 - \vec{r}_1)$$

$$= 4\pi \sum_{\ell',m'} \sum_{\ell'',m''} i^{\ell'-\ell-\ell''} \; I(\ell'm';\ell m;\ell''m'') n_{\ell''}(kr_1) Y_{\ell''}^{m''}(\vec{r}_1)$$

$$\times \; j_{\ell'}(kr_2) Y_{\ell'}^{m'}(\vec{r}_2) \qquad \text{if } |\vec{r}_2 - \vec{r}_1| > r_3 \text{ and } r_1 > |\vec{r}_2 - \vec{r}_3| \qquad (E.11)$$

Since (E.11) involves only $\vec{r}_1$ and $\vec{r}_2$, irrespect of $\vec{r}_3$, thus we can take $\vec{r}_3$ to be located at the origin, and then the conditions for (E.11) reduce to $r_1 > r_2$.

For the case $r_1 < r_2$, we can derive the expansion for the Neumann functions in a similar way by rearranging the arguments in (E.7) and (E.8). The result is:

$$n_\ell(k|\vec{r}_2 - \vec{r}_1|) Y_\ell(\vec{r}_2 - \vec{r}_1)$$

$$= 4\pi \sum_{\ell',m'} \sum_{\ell'',m''} i^{\ell'-\ell-\ell''} \; I(\ell'm';\ell m;\ell''m'') \; j_{\ell''}(kr_1) Y_{\ell''}(\vec{r}_1)$$

$$\times \; n_{\ell'}(kr_2) Y_{\ell'}^{m'}(\vec{r}_2) \qquad \text{if } r_1 < r_2 \qquad (E.12)$$

EXPANSION THEOREM FOR $Y_1^0(\vec{r}_A)/r_A^2$

With the expansion for the Neumann function (Appendix E), we have:

$$\eta_\ell(k|\vec{x}_i-\vec{R}_{ij}|)Y_\ell^m(\vec{x}_i-\vec{R}_{ij})$$

$$= 4\pi \sum_{\ell',m'} \sum_{\ell'',m''} i^{\ell'-\ell-\ell''} \; I(\ell''m'';\ell m''\ell'm') \; \eta_{\ell''}(kR_{ij})Y_{\ell''}^{m''}(\vec{R}_{ij})$$

$$\times j_{\ell'}(kx_i)Y_{\ell'}^{m'}(\vec{x}_i) \qquad \text{if} \quad \vec{x}_i < \vec{R}_{ij} \qquad (F.1)$$

Since, as $k \to 0$, we have:

$$\eta_\ell(kx) \to - (2\ell-1)!!/(kx)^{\ell+1}$$

and
$$j_\ell(kx) \to - (kx)^\ell/(2\ell+1)!!$$

where $n!! = n(n-2)(n-4)\ldots1$

and $(-1)!! = 1$

Thus, as $k \to 0$, equation (F.1) becomes:

$$- \{ (2\ell-1)!!/(k|\vec{x}_i-\vec{R}_{ij}|)^{\ell+1} \} \ Y_\ell^m(\vec{x}_i-\vec{R}_{ij})$$

$$= 4\pi \sum_{\ell',m'} \sum_{\ell'',m''} i^{\ell'-\ell-\ell''} \ I(\ell''m'';\ell m;\ell'm') \ \{ - \frac{(2\ell''-1)!!}{(kR_{ij})^{\ell''+1}} \ Y_{\ell''}^{m''}(\vec{R}_{ij})$$

$$\times \frac{(kx_i)^{\ell'}}{(2\ell'+1)!!} \ Y_{\ell'}^{m'}(\vec{x}_i)\} \qquad\qquad \text{if} \quad x_i < R_{ij}$$

Multiplying $k^{\ell+1}$ on both sides and taking $k\to 0$, then the only nonvanishing term on the RHS is the one with $\ell''=\ell'+\ell$, and we have:

$$Y_\ell^m(\vec{x}_i-\vec{R}_{ij})/|\vec{x}_i-\vec{R}_{ij}|^{\ell+1}$$

$$= 4\pi \sum_{\ell',m'} \sum_{m''} i^{-2\ell} I(\ell'+\ell,m'';\ell,m;\ell',m') \times \frac{(2\ell'+2\ell-1)!!}{(2\ell-1)!!(2\ell'+!)!!}$$

$$x_i^{\ell'}/R_{ij}^{\ell'+\ell+1} \ Y_{\ell'}^{m'}(\vec{x}_i)Y_{\ell'+\ell}^{m''}(\vec{R}_{ij}) \qquad \text{if} \ x_i<R_{ij} \qquad\qquad (F.2)$$

Now, in the treatment of diatomic molecules, we have centers A and B. Thus, let

$$\vec{R}_{ij} = \vec{R}_A - \vec{R}_B$$

$$\vec{x}_i = \vec{r}_A + \vec{R}_{ij} = \vec{r}_B$$

then $\quad \vec{x}_i - \vec{R}_{ij} = \vec{r}_A$

Substituting in (F.2) and considering the case for $\ell=1$, $m=0$,

$$Y_1^0(\vec{r}_A)/r_A^2 = 4\pi \sum_{\ell',m'} \sum_{m''} i^{-2} \ I(\ell'+1,m'';1,0;\ell',m') \ \frac{(2\ell'+1)!!}{(2\ell'+1)!!}$$

$$\times \ r_B^{\ell'}/R_{AB}^{\ell'+2} \ Y_{\ell'}^{m'}(\vec{r}_B) Y_{\ell'+1}^{m''}(\vec{R}_A-\vec{R}_B) \qquad \text{if } r_B < R_{AB}$$

Since $\vec{R}_A-\vec{R}_B$ is along the z-axis, therefore

$$Y_{\ell'+1}^{m''}(\vec{R}_A-\vec{R}_B) = \delta_{m''0} \ Y_{\ell'+1}^{0}(\vec{R}_A-\vec{R}_B)$$

which implies that the only nonvanishing term in the summation over m' is the one with m'=0. Thus, we have:

$$Y_1^0(\vec{r}_A)/r_A^2 = -\ 4\pi \sum_{\ell'=0}^{\infty} I(\ell'+1,0;1,0;\ell',0) Y_{\ell'+1}^{0}(\vec{R}_A-\vec{R}_B)/R_{AB}^{\ell'+2}$$

$$\times \ r_B^{\ell'} \ Y_{\ell'}^{0}(\vec{r}_B) \qquad \text{if } r_B < R_{AB} \qquad (F.3)$$

Similarly we can prove the expansion theorem for the case $r_A > R_{A0}$ by using (F.12). The result is:

$$Y_1^0(\vec{r}_A)/r_A = 4\pi \sum_{\ell'=1}^{\infty} I(\ell'-1,0;1,0;\ell',0) R_{A0}^{\ell'-1} Y_{\ell'-1}^{0}(\vec{R}_A-\vec{R}_0)$$

$$\times \ Y_{\ell'}^{0}(\vec{r}_0)/r_0^{\ell'+1} \qquad \text{if } r_A > R_{A0} \qquad (F.4)$$

APPENDIX G

EVALUATION OF THE SINE AND COSINE INTEGRALS

In the force and dipole moment calculations, we have
to evaluate the following integrals:

$$\int_{t_1}^{t_2} \frac{f(t)}{t^p(a-t)^q} \, dt$$

where $f(t) = 1$, cost, sint, and p,q are integers.

It can be proved that the evaluations of these kinds
of integrals wind up with the evaluations of the sine and
cosine integrals, namely:

$$\int \cos x/x \, dx \qquad \text{and} \qquad \int \sin x/x \, dx$$

as we shall show below:

(1) q < 0

In this case, we can use the binomial expansion for
$(a-t)^{-q}$. Then, we have:

$$\frac{1}{t^p(a-t)^q} = \sum_{k=0}^{|q|} C_k^{-q} (-1)^k a^{-q-k} t^{-q-p}$$

Thus, $\int_{t_1}^{t_2} \frac{f(t)}{t^p(a-t)^q} = \sum_{k=0}^{|q|} C_k^{-q} (-1)^k a^{-q-k} \int_{t_1}^{t_2} \frac{f(t)}{t^{p+q}} dt$

(2) p < 0

In this case, we change the variable t to x: x=a-t. Then, we have:

$$cost = \cos(a-x) = \cos a \cos x + \sin a \sin x \quad etc.$$

and $\quad t^p(a-t)^q = (a-x)^p x^q$

Thus $\quad \displaystyle\int_{t_1}^{t_2} \frac{cost}{t^p(a-t)^q} \, dt = \int_{a-t_1}^{a-t_2} \frac{\cos a \cos x + \sin a \sin x}{x^q(a-x)^p} \, dx \quad etc.$

which can be evaluated just like Case (1).

(3) q > 0, p > 0

Integrating by parts and using the following identity:

$$\int \frac{dt}{t^p(a-t)^q} = a^{1-p-q} \left\{ \sum_{\substack{s=0 \\ s \neq p-1}}^{p+q-2} C_s^{p+q-2} / (p-s-1) \int \left(\frac{a-t}{t}\right)^{p-s-1} dt \right.$$

$$\left. C_{p-1}^{p+q-2} \log\left|\frac{a-t}{t}\right| \right\}$$

we wind up with the integrals encountered in Case (1) or Case (2) according to whether p-s-1 is positive or negative.

Thus, for all cases, we winds up with the evaluation of integrals:

$$\int_{x_1}^{x_2} \cos x / x^m \, dx \qquad and \qquad \int_{x_1}^{x_2} \sin x / x^m \, dx$$

For negative values of m, these can be reduced to the evaluation of sine and cosine functions by the formula:

$$\int x^{-m}\cos x \; dx = x^{-m}\sin x + m \int x^{-m-1}\sin x \; dx$$

$$\int x^{-m}\sin x \; dx = -x^{-m}\cos x - m \int x^{-m-1}\cos x \; dx$$

For positive values of m, we have similar relations:

$$\int \cos x/x^m \; dx = - \cos x/ (m-1)x^{m-1} \; - \frac{1}{m-1} \int \sin x/x^{m-1} \; dx$$

$$\int \sin x/x^m \; dx = - \sin x/ (m-1)x^{m-1} \; + \frac{1}{m-1} \int \cos x/x^{m-1} \; dx$$

$$(m \geqslant 2)$$

which reduces to the evaluation of the integrals:

$$\int_{x_1}^{x_2} \cos/x \; dx \qquad \text{and} \qquad \int_{x_1}^{x_2} \sin x/x \; dx$$

These two integrals can be evaluated as:

$$\int_{x_1}^{x_2} \cos/x \; dx = ci(x_2) - ci(x_1)$$

$$\int_{x_1}^{x_2} \sin/x \; dx = si(x_2) - si(x_1)$$

where $ci(x)$ and $si(x)$ are defined by: .

$$ci(x) = C + \log x + \int_0^x (\cos t - 1)/t \; dt$$

$$\text{si}(x) = \int_0^x \sin t/t \, dt - \pi/2$$

where C is the Euler constant 0.57....

The functions ci(x) and si(x) can be computed with a subroutine called SICI which is stored in the IBM Scientific Subroutine Package:

For $x \leqslant 4$ and $t=16-x^2$:

$$\{\text{si}(x)+\pi/2\}/x = 4.395509E-1 + 1.964882E-2 \ t + 6.939889E-4 \ t^2$$
$$+ 1.374168E-5 \ t^3 + 1.568988E-7 \ t^4$$
$$+ 1.753141E-9 \ t^5 + \varepsilon$$

with $|\varepsilon| < 8.2E-8$

$$\{-\text{ci}(x)-C-\log|x|\}/x^2 = 1.315308E-1 + 4.990920E-3 \ t$$
$$+ 1.185999E-4 \ t^2 + 1.725752E-6 \ t^3$$
$$+ 1.584996E-8 \ t^4 + 1.386985E-10 \ t^5 + \varepsilon$$

with $|\varepsilon|< 5.6E-9$

For $x>4$ and $t=4/x$:

$$\text{si}(x) = - (4/x) \{\cos x \ P(x) + \sin x \ Q(x) + \varepsilon\}$$
$$\text{ci}(x) = (4/x) \{\sin x \ P(x) - \cos x \ Q(x) + \varepsilon\}$$

where $|\varepsilon| < 2.3E-8 \ x^{-1}$

and $P(x) = 2.500000E-1 - 6.646441E-1 \ t - 3.122418E-2 \ t^2$
$$- 3.764000E-4 \ t^3 + 2.601293E-2 \ t^4 -7.945556E-3 \ t^5$$
$$- 4.400416E-2 \ t^6 + 7.902034E-2 \ t^7 - 6.537283E-2 \ t^8$$
$$+ 2.819179E-2 \ t^9 - 5.108699E-3 \ t^{10}$$

$Q(x) = 2.583989E-1 + 6.250011E-2 \ t - 1.134958E-5 \ t^2$
$$- 2.314617E-2 \ t^3 -3.332519E-3 \ t^4 +4.987716E-2 \ t^5$$
$$-7.261642E-2 \ t^6 + 5.515070E-2 \ t^7 -2.279143E-2 \ t^8$$
$$+ 4.048069E-3 \ t^9$$

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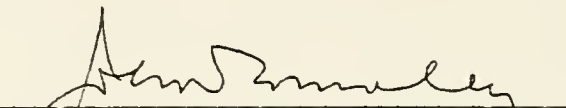
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BIOGRAPHICAL SKETCH

Choy Hing Li was born July 3, 1946 in Hong Kong. In June, 1965, he was graduated from Perth Street Government Middle School in Hong Kong. He attended Chung Chi College, the Chinese University of Hong Kong, with a four-year government scholarship. In June, 1969, he received the degree of Bachelor of Science(honour) with a major in Physics. In September, 1969, he came to the United States and enrolled in the Graduate School of the University of Florida as a student in the Department of Physics. Throughout the period of graduate study, he has been employed as either a teaching assistant or a research assistant.

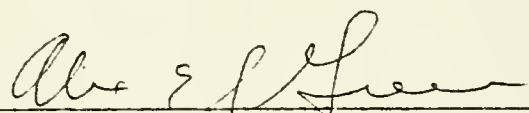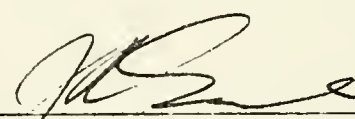Choy Hing Li is married to the former Mei-zu Lin. He is a member of the Sigma Pi Sigma.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

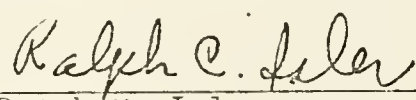John W.D. Connolly, Chairman
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Alex E.S Green
Graduate Research Professor of
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John R. Sabin
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This dissertation was submitted to the Department of Physics and Astronomy in the College of Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December, 1975

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